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SYNTHESIS AND CHARACTERIZATION OF POLY(AMIDE-SULFONAMIDES): NEW CANDIDATES FOR REVERSE OSMOSIS MEMBRANES.

THEVARAK ROCHANAPRUK

MAY , 1985

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

APPROVED:

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ABSTRACT

Commercially available aromatic diamines such as 4,4'-diamino diphenyl ether and 4,4'-diamino diphenyl methylene were treated with N-acetylsulfanilyl chloride to give the amino-sulfonamido-acetanilide derivatives. These derivatives were treated with 6 M hydrochloric acid to give the diamine monomers containing a preformed sulfonamide linkage. These monomers were polymerized with various diacid chlorides using a low temperature solution technique. Polymerizations using the Yamazaki reaction have also been investigated.

The polymers obtained were characterized using infrared spectroscopy, thermal gravimetric analysis and differential scanning calorimetry.

ABBREVIATIONS

ABSC	=	N-acetamidobenzene sulfonyl chloride (N-acetylsulfanilyl chloride)
Ac	=	Acetyl
DMAc	=	N,N-dimethylacetamide
DMF	=	N,N-dimethylformamide
DSC	=	Differential Scanning Calorimetry
IR	=	Infrared
m.p.	=	melting point
Me	=	Methyl
NMR	=	Nuclear Magnetic Resonance
$\eta_{inh.}$	=	Inherent viscosity
NMP	=	N-methyl-2-pyrrolidone
PDT	=	Polymer decomposition temperature
Ph	=	Phenyl
Py	=	Pyridine
Tg	=	Glass transition temperature
TGA	=	Thermal Gravimetric Analysis
TLC	=	Thin Layer Chromatography

ACKNOWLEDGEMENTS

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1.0 INTRODUCTION.

Since the early 1970's, reverse osmosis has undergone rapid development as a process for the desalination of brackish water (1). In reverse osmosis, saline water is placed in contact with a suitable membrane at a pressure exceeding the osmotic pressure of the solution. Fresh water, or water with lower salt content, permeates the membrane and is collected for use. A concentrated brine is discharged from the high pressure side of the membrane as a waste stream. Reverse osmosis development has been directed primarily toward the production of fresh water from natural brackish water. However, reverse osmosis units have also been tested in a variety of other water and waste treatment applications, including water recovery and concentration of wastes from sewage plants. For a membrane with a given specific permeability, the fresh water output or flux of a reverse osmosis device is directly proportional to the membrane thickness. Membrane area can be maximized and thickness minimized in the hollow fiber form. Fine hollow fibers provide a thin, self supporting membrane with a very high surface to volume ratio desirable for reverse osmosis.

The important properties for a reverse osmosis membrane are flux rate, salt rejection and durability. The water permeation rate or flux rate of the reverse osmosis membranes can be expressed as gallons per day per square foot (g.f.d.) or cubic meter per square meter per day ($m^3/m^2/day$) based on the outside diameter of the membrane. The selectivity of a reverse osmosis membrane is often expressed as the % salt rejection (SR), which is defined by the equation:

$$\% \text{ SR} = (Cf-Cp)/Cf \times 100$$

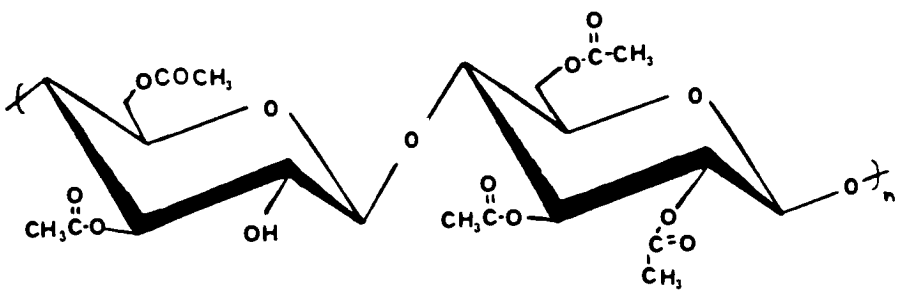
where Cf = salt concentration in feed water,

Cp = salt concentration in the permeate.

The salt rejection required in a revese osmosis application depends upon the proposed water use. Generally, for the production of potable water, a permeate concentration of <500 ppm is desired. Thus, a salt rejection on the order of 85% - 95% is required for brackish water desalination (1000-5000ppm) and >98.5% for sea water desalination (35,000 ppm).

The rejection of a reverse osmosis membrane varies with the solute composition in the feed water. Multivalent ions are generally rejected better than the monovalent ions. Another factor which influences the salt rejection is pH. The durability of a reverse osmosis membrane is usually influenced by both the membrane properties and the nature of the system in which it is operating. The decline in performances of the membrane can be attributable to membrane compaction, fiber collaspe, fouling (slime or scale), chemical and biological degradation.

One of the most widely used reverse osmosis membranes to date is cellulose di-triacetate 1 .



1

As demonstrated by Reid and Breton (2), cellulose acetate membranes showed salt rejection ranges of 86 - 99% of electrolytes. The electrolytes used were the chlorides of sodium, magnesium and calcium. In addition, ammonia, sodium bromide and sodium fluoride were tested.

The behavior of cellulose acetate as a reverse osmosis membrane can be best explained by examining its internal structure. In addition to the amorphous region, cellulose acetate's internal structure posesses a moderate degree of crystallinity. As suggested by Fuller and Pape (3), the crystalline regions in cellulose acetate have strong intermolecular forces, large enough to restrict the Brownian motion and hold a large percentage of polymer chains in a highly ordered region. Reid and Breton (2) proposed that, when water molecules are introduced into cellulose acetate, they are concentrated in the amorphous regions. It is postulated that they are hydrogen bonded to the carbonyl oxygens of the acetyl group, thereby filling the voids with bound water. In a structure such as this, it is proposed that two different diffusion mechanisms occur. Firstly, the ions and molecules that cannot enter into hydrogen bonding are transported across the membrane by hole type diffusion. That is, their diffusion depends upon the probability of hole formation in the membrane. Filling the pores of cellulose acetate with tightly bound water reduces the probability of hole formation, thereby reducing the diffusion of this type. Secondly, those ions and molecules that can combine

with the membrane through hydrogen bonding and can fit into the bound water structure, are presumed to be transported across the membrane by alignment of the hydrogen bonds with the membrane.

After these molecules combine with one side of the membrane, they migrate across by transferring from one hydrogen bonding site to another and are finally discharged from the other side of the membrane. The hydrogen bonding concept for the semi-permeability of cellulose acetate was supported by the fact that using electrolytes such as sodium chloride and sodium bromide, which can enter into hydrogen bonding with cellulose acetate, were effectively rejected by the membrane. On the other hand, sodium fluoride used as the electrolyte, was found to be less rejected by the membrane. This can be explained by the fact that the smaller fluoride ion can enter into hydrogen bonding and diffuse at a greater rate.

A low rejection would be expected for those solutes that can enter into water-cellulose acetate structure through hydrogen bonding. Ammonia is an example of this type of solute. It was found that the permeability for ammonia was 30% or about one third of that for sodium chloride (2).

Table I: Semipermeability of Cellulose Acetate Membrane to Aqueous Solution of Various Electrolytes (2).

Pressure on Membrane (psi)	Electrolyte	Concentration	(%) Salt Rejection
850	NaCl	0.11 M	96
850	Na_2SO_4	0.018 M	97
800	NH_3	0.04 M	30
800	ocean water	4%	96
800	NaF	0.0012 M	86
850	NaBr	0.0012 M	93
715	$MgCl_2$	0.031 M	99

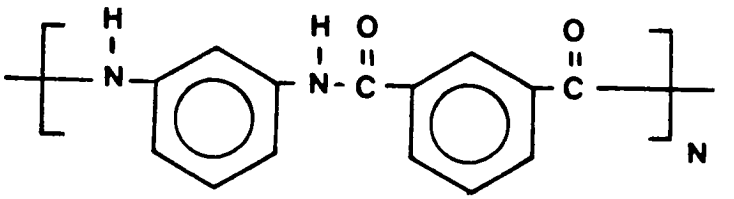
After long term usage, cellulose acetate membranes show poor chemical and mechanical stability (4). Because of this, many new polymers have been developed and evaluated as candidates for reverse osmosis membranes. Polymers having significant desalination properties are polyacrylonitrile, poly(vinylene carbonate), Nylon 6-6, poly(isobutyl vinyl ether), polytetrahydrofuran and a copolymer of ethylene dimethacrylate and hydroxyethyl methacrylate. In addition, a polymer blend of ethyl cellulose and poly(acrylic acid) also has good desalination properties (5).

1.1 Polyamides.

Polyamides with the general structure of ~~-(-HN-R-NH-CO-R'-CO-)-~~ have been developed and evaluated as candidates for reverse osmosis membranes. These polymers can be prepared using a low temperature solution polymerization technique or an interfacial polycondensation method (6,7,8).

Among the new polyamides synthesized, poly(m-phenylene isophthalamide) 2 gave a promising performance as a reverse osmosis membrane.

As was demonstrated by R. McKinney and J.H. Rhodes (9), this polymer gave a 98.4% sodium chloride rejection, with an electrolyte concentration of 5000 ppm and a pressure of 1000 psi. The flux rate for water was 2.5 gal/ft^2/day.



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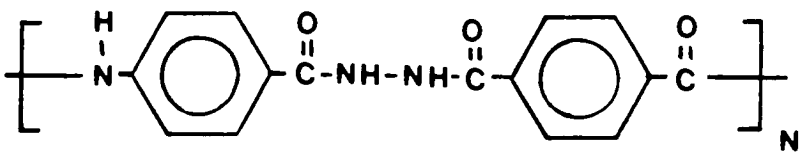
Poly(m- phenylene isophthalamide) can be prepared by reacting m-phenylene diamine with isophthaloyl chloride using a low temperature solution or interfacial condensation method.

The structure of this polymer is kinked due to the meta linkages of the amide groups in the polymer backbone. These kinked regions form the amorphous region in the polymer. One would expect poly(m-phenylene isophthalamide) therefore to be highly amorphous, and have many empty volumes or voids in the polymer membrane. Since there are fewer regions of crystallinity (ordered region) in this polymer as

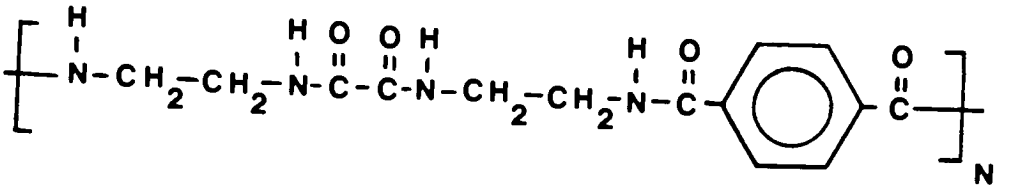
compared to cellulose acetate, 2 should therefore have a lower water diffusion rate than cellulose acetate. Experimentally this was found to be the case (9).

On the other hand, linear polymers, for example polyterephthalamide of p-amino benzhydrazide 3 , gave a salt rejection of 98.0% and flux rate of 8.7 gal/ft^2/day using a pressure of 1000 p.s.i.. Sodium chloride with a concentration of 5,000 ppm was used as the electrolyte (9).



3

Another polyamide that has an unusual structure and properties is copolyoxamide 4 . This polymer possesses both a highly hydrophilic oxamide linkage and a hydrophobic aromatic diacid unit. This combination provides both high water permeability and high mechanical strength in aqueous solvents (4).



4

The membrane from this polymer (4) was prepared by casting a 10% (w/v) polymer solution in N,N-dimethylacetamide containing 6.6% (w/v) lithium chloride on a glass plate, heated in an oven to remove the solvent, and gelled in water. Scanning electron microscopy of this membrane showed the structure to consist of voids ranging in size from less than 1μm to 100μm. In addition, regular voids of 200-300 A in diameter were also observed. This membrane showed sodium chloride rejection values of 85 - 99% and high rate of water diffusion.

Tirrel and Vogl (4) also found structural differences in membrane cast from trifluroacetic acid and N,N-dimethylacetamide - lithium chloride mixtures. Electron micrograph cross sections of membrane cast from N,N-dimethylacetamide - lithium chloride mixtures, showed two dense surface layers connected by a regular array of capillaries, 4 - 5 μm in diameter. This structure is a unique feature of this system and is comparable to the structure of a cellulose acetate membrane (4).

Membranes cast from a trifluroacetic acid - polymer solution, consist of voids ranging in size from less than 1μm to 100μm (approximately the entire film thickness). In addition , regular voids of 200-300 A in diameter were also observed in the solid portions of the membrane. Membranes cast from N,N-dimethyl-acetamide - lithium chloride mixtures showed a better flux rate than those cast from trifluroacetic acid (4).

The effect on the membrane flux rate in the presence of inorganic salts has also been investigated in detail. As demonstrated by M.A Kraus and co-workers (10), a typical aromatic polyamide membrane cast under certain conditions from a binary solution, i.e. a solution containing only the polymer and the solvent,

gave a different flux rate than a membrane cast from a solution containing inorganic salts. The membrane cast from a binary solution exhibited a water flux rate of 0.85 $m^3/m^2/day$. Membranes prepared under the same conditions using the same polymer mixed with inorganic salts such as lithium chloride or lithium perchlorate exhibited fluxes as high as 250 - 600 $m^3/ m^2/day$. The effect of various inorganic salts on the flux rate of the aromatic polyamide membranes are summarized in Table II.

[a]

Table II: The Effect of Inorganic Salts on Membrane Flux and % Salt Rejection.

Salt	Salt Concentration		% Rejection		Membrane Flux
	% (w/v)	Molarity	Urea	NaCl	($m^3/m^2/day$)
LiCl	5	1.2	77	-	34
$LiClO_4$	10	0.47	78	-	51
$LiClO_4$	5	0.94	85	-	42
$ZnCl_2$	10	0.73	83	99	46
$Mg(ClO_4)_2$	5	0.22	80	96	38
$Mg(ClO_4)_2$	10	0.45	72	96	63
$ZnCl_2$ + Py.HCl	10 20	0.73 1.73	88	99	92.4
$Mg(ClO_4)_2$ + Py.HCl	10 20	0.45 1.73	80	99.9	189

[a] Membrane consisted of a 1:1 mixture of poly m-and p-phenylene isophthalamide.

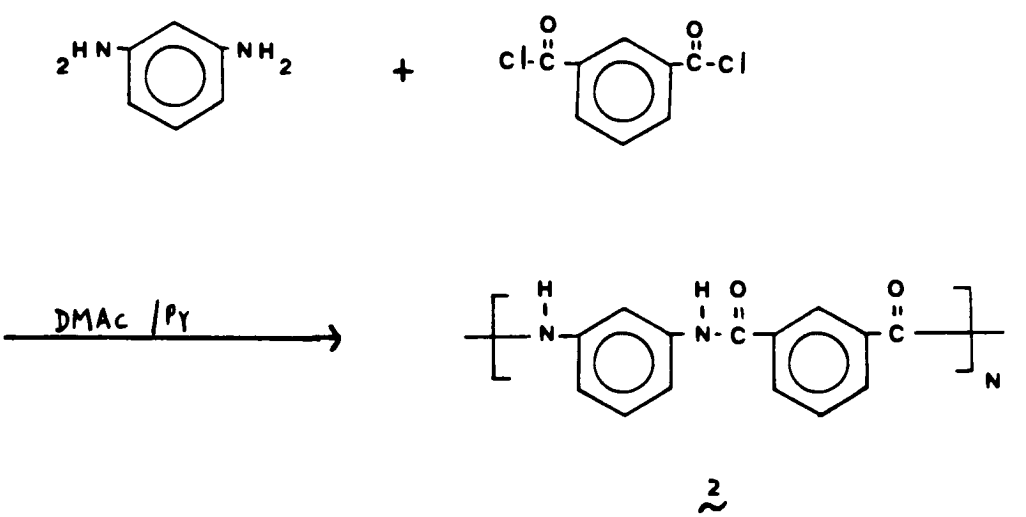
The combination of magnesium perchlorate/ pyridinium hydrochloride with 2 gave the best results in % salt rejection and water flux rate. Many experimental facts indicate that the "salt effect" is primarily due to the changes in the solvent activity. Evidence was obtained from the Nuclear Magnetic Resonance spectra of the polymer solutions. It was observed that a lithium chloride - aromatic polyamide interaction caused a down field shift in the NMR signal of the amide protons of the polymer (11). It was also found that under certain conditions,such as temperature, pressure and time, the amount of the solvent lost from a cast membrane before coagulation decreased with increased additive concentration. This is due to a decrease in the solvent's vapour pressure. By increasing the additive concentration, the membrane will contain a higher solvent to polymer ratio at the instant of coagulation, resulting in a more open structure.

In addition, solvent evaporation will lead to an asymmetrical structure already in the membrane, as was shown by scanning electron microscopy (12). The asymmetrical structure should be more pronounced with a higher additive concentration. As the solvent evaporates, the salt-polymer concentration near the solution-air interface increases thus impeding further

evaporation of the solvent. The diffusion is slow in the highly viscous solution, and the salt-polymer concentration equalization is slow relative to evaporation rate. An asymmetrical structure results upon coagulation, since the polymer concentration is higher at the upper surface and lower within the membrane. Both the evaporation and coagulation phenomena are important in determining the final structure of the aromatic polyamide membranes.

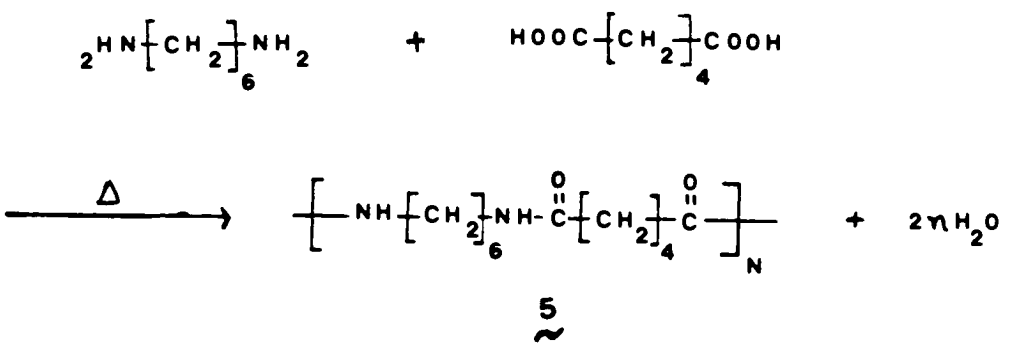
The effects of inorganic salts in solution of aromatic polyamides need further study.

Polyamides can be prepared by an interfacial or low temperature solution polymerization techniques. An example is the synthesis of poly(m-phenylene isophthalamide) 2 .



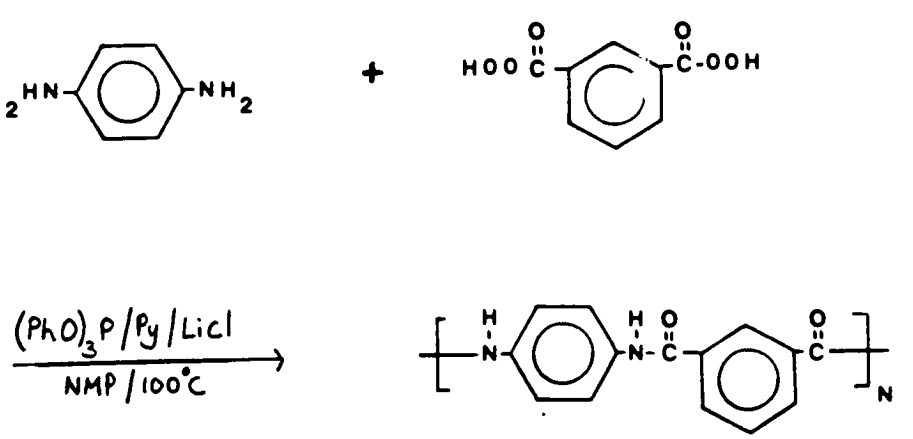
2

Polyamides can also be prepared by the reaction between a diamine and a dicarboxylic acid using the melt polymerization technique, for example the preparation of Nylon 6-6, 5 .



5

A new method for polyamide synthesis was reported by Yamazaki and co-workers (13). A high molecular weight polyamide 6 was obtained (ηinh. = 1.5 dL/g in conc. sulfuric acid) when p-phenylene diamine was reacted with isophthalic acid in the presence of triphenyl phosphite, pyridine and lithium chloride.



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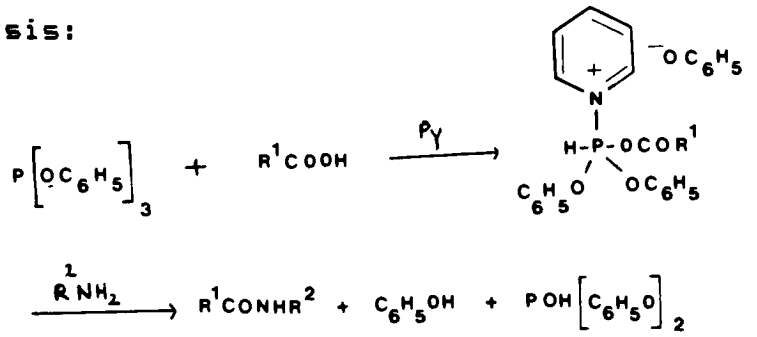
It is postulated that the reaction proceeded via the N-phosphonium salts of pyridine followed by aminolysis:



Imai and co-workers (14) have also prepared various aromatic and aliphatic polyamides using the Yamazaki reaction. The polymers obtained gave high inherent viscosity values. For example the polymer obtained from the reaction between 4,4'-oxydianilie and terephthalic acid gave an inherent viscosity value of 2.39 dL/g in concentrated sulfuric acid. Using isophthalic acid, the polymer obtained gave an inherent viscosity value of 1.98 dL/g, suggesting high molecular weight materials.

Important factors in the Yamazaki reaction are temperature, solvent, monomer concentration, metal salt type and reaction time. The best solvent for this rection was found to be N-methyl-2-pyrrolidone with the monomers concentration being 0.6 mole.

The results for the polymerization of p-aminobenzoic acid using the Yamazaki reaction are summarized in Table III.

Table III: Polycondensation Reaction of p-Amino Benzoic Acid Using Triphenyl Phosphite in Various Solvent Systems containing 4% (w/v) Lithium Chloride.[a]

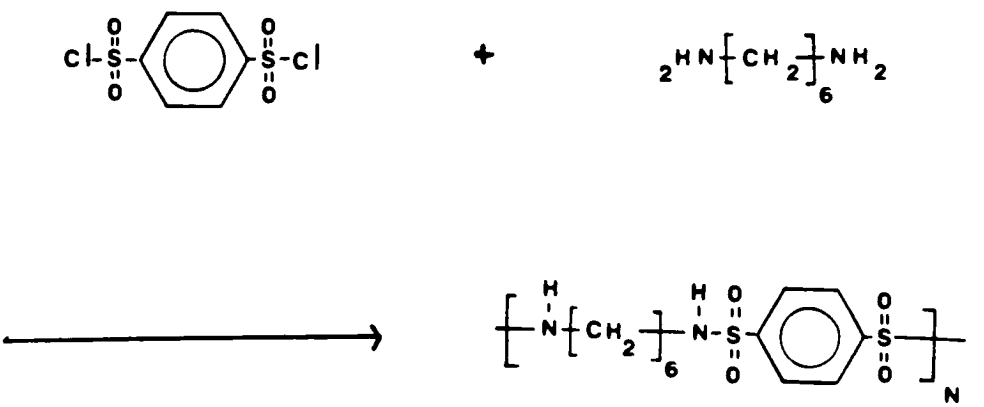
Solvent System (ml/ml)	% Yield	Inherent Viscosity (dL/g) c= 0.5 g/dL[b]
Dioxane/Pyridine (40/10)	21	0.07
DMF/Pyridine (40/10)	11	0.08
DMAc/Pyridine (40/10)	99	0.71
Pyridine (50)	100	0.21
NMP/Pyridine (10/40)	100	0.29
NMP/Pyridine (20/30)	100	1.21
NMP/Pyridine (30/20)	100	1.57
NMP/Pyridine (40/10)	100	1.27
NMP/Pyridine (45/5)	100	1.26

a) Monomer concentration = 0.4 mole, triphenyl phosphite concentration = 1 mole/mole of monomer, temperature = 100°C, reaction time = 6 hrs.

b) measured in concentrated sulfuric acid at 30°C.

1.2 Polysulfonamides

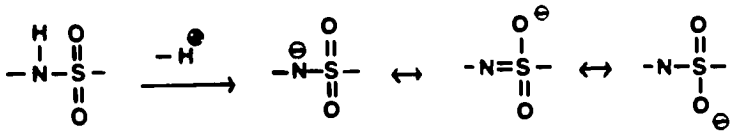
Polysulfonamides with the general structure ($-SO_2-R-SO_2-NH-R'-NH-$) can be prepared in high molecular weight by the reaction of a disulfonyl chloride and a diamine using an interfacial polycondensation technique. A series of high molecular weight polysulfonamides were prepared from the reaction of an aromatic disulfonyl chloride with various aliphatic diamines by S.A. Sundet and co-workers (14). An example of this is the rection between 1,6 hexamethylene diamine with benzene disulfonyl chloride to form a polysulfonamide 7 .



7

Using an interfacial polymerization technique, polymers with the inherent viscosity ranging from 0.1-2.62 dL/g were obtained. Higher molecular weight polymers were obtained when sodium carbonate rather than sodium hydroxide was used as the acid acceptor. This was attributed to a reduction of the sulfonyl chloride hydrolysis at the lower pH. In addition, the carbonate may be acting to "salt out" the diamine more rapidly into the organic phase.

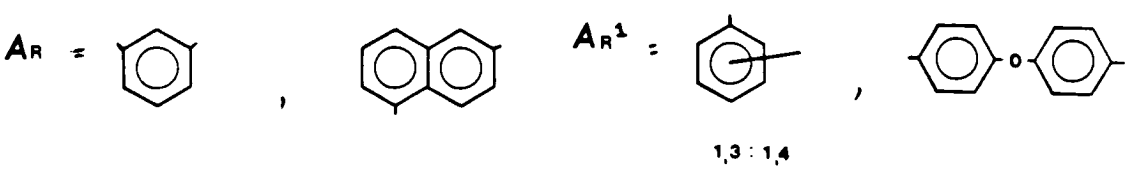
In the synthesis of polysulfonamides, pH control is important. Sulfonamides dissolve in 10% sodium hydroxide solution because of the acidity of the sulfonamide group.



Thus interfacial polymerizations carried out at higher pH levels cause the formation of the anion ($-SO_2-\overset{\ominus}{N}-$) which can be sulfonated in sufficient amounts to form a branched and/or insoluble polymers. This phenomena was observed in the reaction of 1,2-ethylene diamine and 1,3-benzenedisulfonyl chloride, using sodium hydroxide as the acid acceptor.

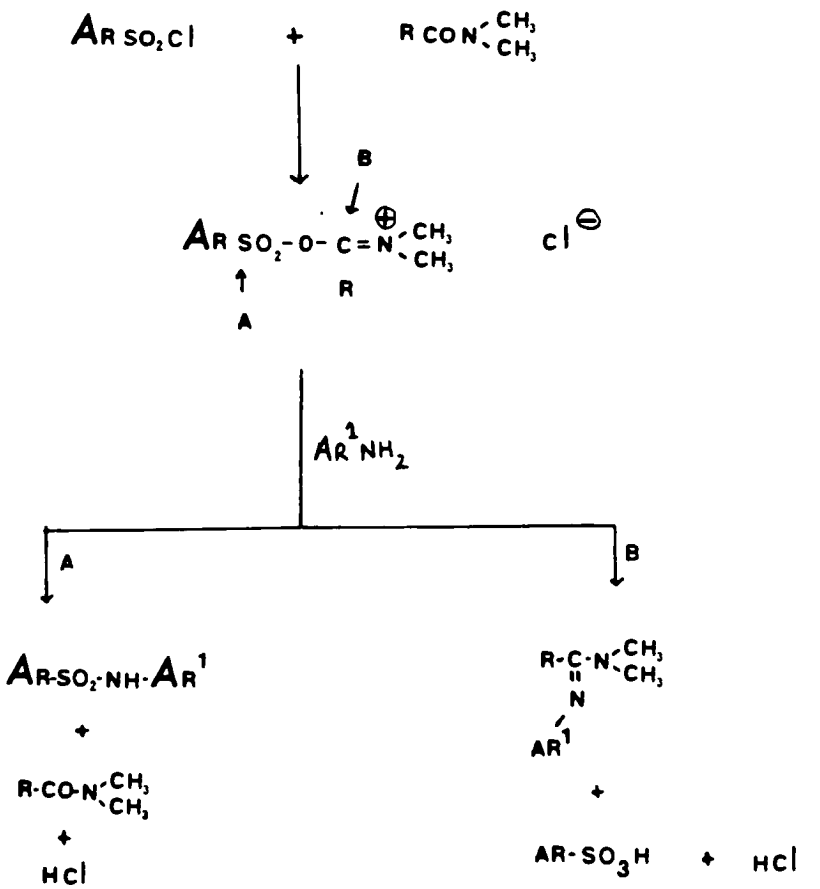
Sundet and co-workers (14) were unable to prepare wholly aromatic high molecular weight polysulfonamides due to the low basicity of the aromatic diamines and the lower reactivity of sulfonyl chlorides as compared to

carboxylic acid chlorides. Low molecular weight polysulfonamides were also obtained by C.S. Marvel and his co-workers(15) by reacting aromatic diamines with aromatic disulfonyl chlorides. The polymers obtained using solution polymerization technique with N,N-dimethylacetamide or tetramethylene sulfone as the solvents, gave a range of inherent viscosity between 0.02-0.19 dL/g.



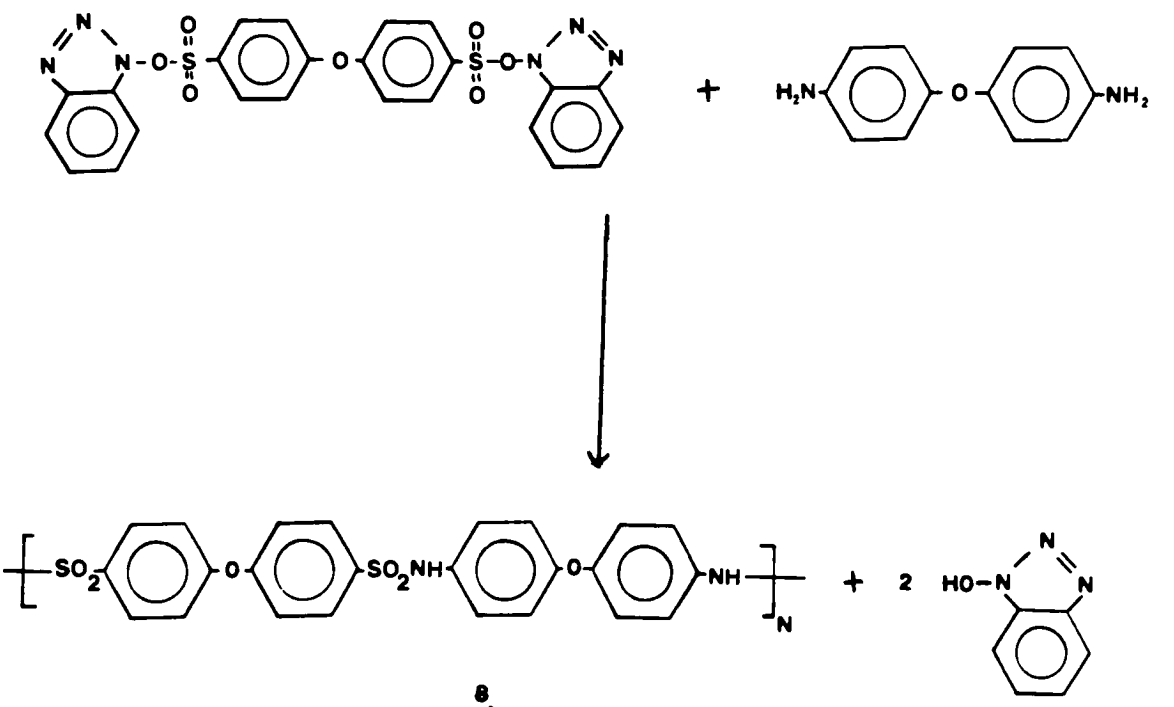
Imai and co workers (16), were able to synthesize wholly aromatic polysulfonamides using a low temperature polymerization technique. Unlike Marvel and co-workers (15), 2-methyl pyridine was used as the solvent and pyridine as the acid acceptor in their reactions. This combination of solvent and acid acceptor gave a polysulfonamide with an inherent viscosity of 0.43dL/g with 99% yield. The formation of high molecular weight polymer was attributed to the

solvent's ability to sufficiently dissolve or swell the polymer thus permitting complete polymerization. Polymerizations using amide type solvents such as N,N-dimethylacetamide (a good solvent for aromatic polysulfonamides), produced inferior results. Aromatic sulfonyl chlorides are known to react with N,N-dialkylamides to give the ammonium salt (17). The reaction of which, produced a mixture of sulfonamides (through path A) and the amidines (through path B) in the following equation.



It was assumed that N,N-dimethylacetamide reacted with the aromatic disulfonyl chlorides to form the sulfonic acids which resulted in the termination of the polycondensation and yielded only low molecular weight polysulfonamides.

Polysulfonamides can also be prepared using active di-1-benzotriazoyl disulfonate and aromatic diamines under mild condition. It was shown by L.A. Paquette (19) that 1-hydroxy-2(1H) pyridone benzenesulfonate reacts with an amine to form the exclusively sulfur-oxygen cleavage products. Reacting a di-benzotriazoyl disulfonate with an aromatic diamine yielded a polysulfonamide 8 (20).

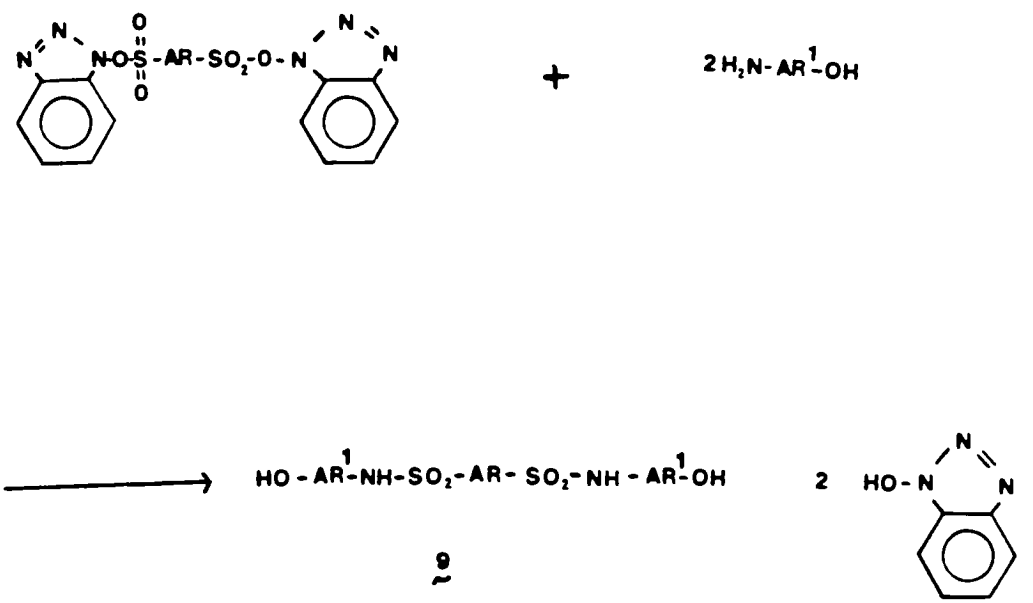


8

Various solvents such as N-methyl-2-pyrrolidone and hexamethyl phosphoramide were used in the preparation of 8. The acid acceptors varied ranging from sodium carbonate, pyridine to N-ethylmorpholine.

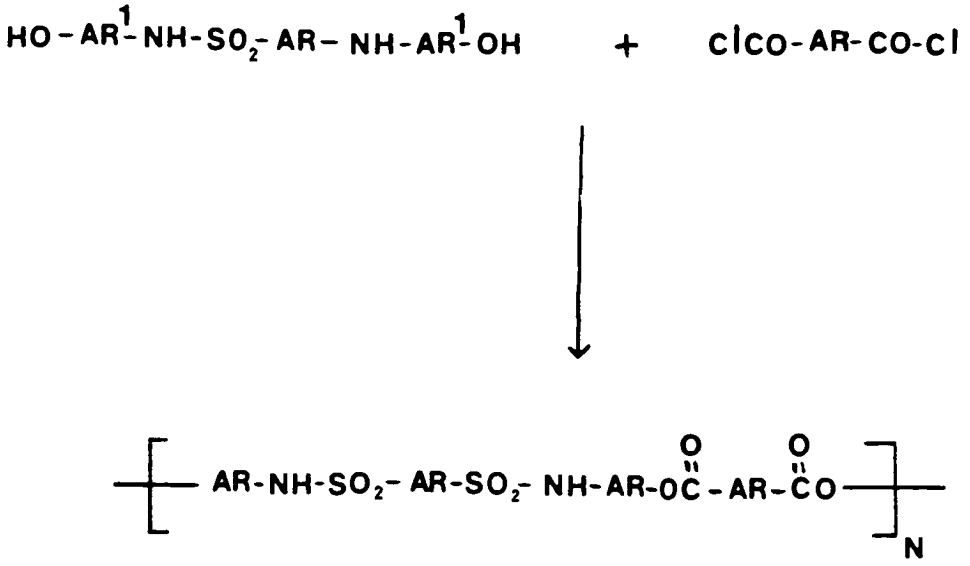
For the polycondensation of di-1-benzotriazoyl disulfonate with bis(4-aminophenyl ether), the solvent and acid acceptor combination which gave the highest inherent viscosity (0.55 dL/g) was hexamethyl phosphoramide and 2,6-dimethyl pyridine.

High molecular weight polysulfonamide esters 10 have also been prepared (21). Reacting di-1-benzotriazoyl disulfonate with an aminophenol, a diphenol monomer 9 was obtained by the cleavage of the sulfur-oxygen bond.



9

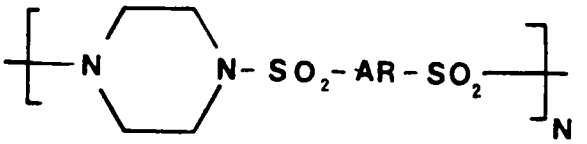
The diphenol 9 was reacted with an aromatic di- acid chloride such as terephthaloyl chloride, using tetraethyl ammonium chloride as a catalyst, to give 10 in good yield.



10

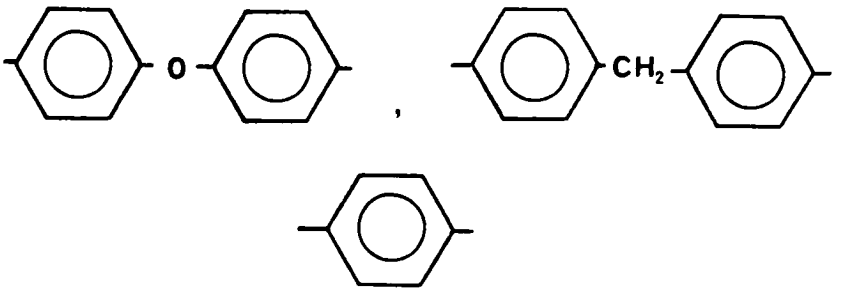
The polymerization was carried out using an interfacial technique. The best results were obtained when a chloroform/water solvent mixture was used. The polymer obtained in this case had an inherent viscosity of 0.86 dL/g in N,N-dimethylacetamide.

In general, aromatic polysulfonamides exhibit lower thermal stability than that of aromatic polyamides. R.C.Evers and G.F.L. Ehlers (22) found that piperazine aromatic polysulfonamides 11 decomposed around 300-350°C.



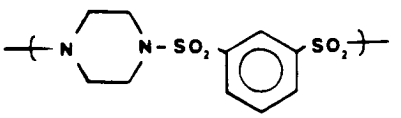
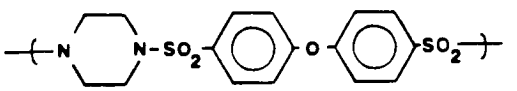
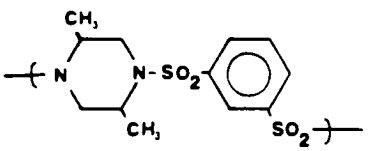
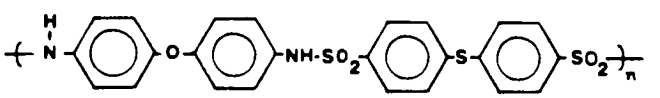
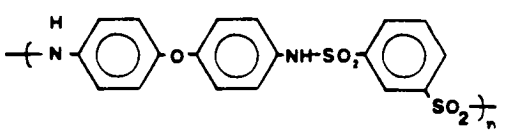
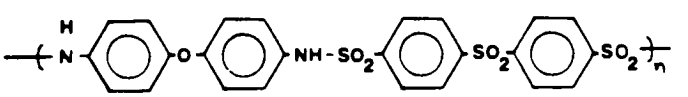
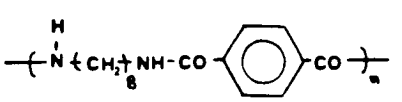
11

AR =



Polyamides showed a higher decomposition temperature around 410-450°C (6). The lack of thermal stability shown by polysulfonamides can be attributed to the nitrogen-sulfur (N-S) bonds in the polymer backbone. The thermal stability of polyamides and polysulfonamides are summarized in Table IV.

Table IV: Thermal Properties of Polyamides (6) and Polysulfonamides (22) under Nitrogen Atmosphere.

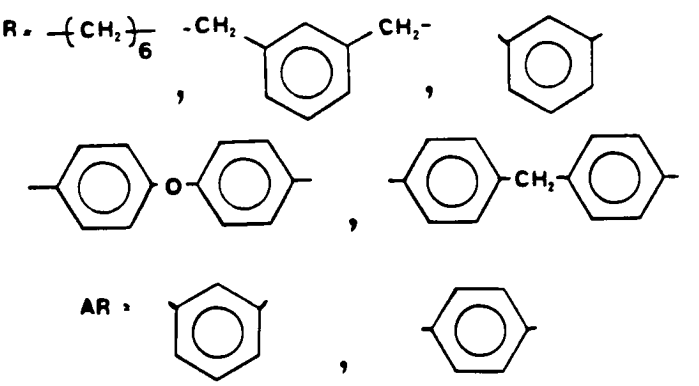
Polymer	Inherent Viscosity	TGA curve[a] (°C)
	0.07	350
	0.12	355
	0.07	310
	0.25	400
	1.27	380
	0.40	395
	N/A	470

a) Polymer decomposition temperature.

1.3 Poly(amide-sulfonamides).

Poly(amide-sulfonamides), 12, with the general structure (NH-CO-R-SO_2-NH-R'-) can be prepared by reacting either meta- or para-chlorosulfonylbenzoyl chloride with various diamines using an interfacial polymerization technique (23).

12



The polymers obtained had inherent viscosities ranging from 0.14-0.18 dL/g. Nearly all of the polymers were soluble in a wide range of organic solvents such acetone, m-cresol and N,N-dimethylacetamide.

Poly(amide-sulfonamides) were also soluble in basic and acidic solvents such as formic acid, glacial acetic acid, pyridine and 10% aqueous sodium hydroxide solution.

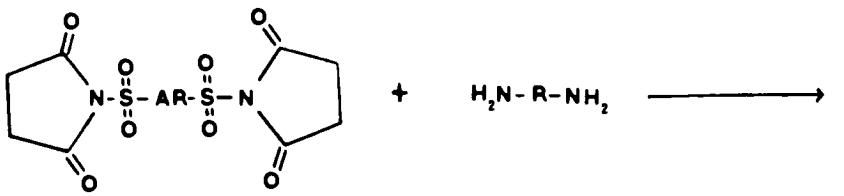
The thermal gravimetric analysis curve of the aliphatic poly(amide-sulfonamides) showed a decomposition at 320-360°C in a nitrogen atmosphere. Some aliphatic poly(amide-sulfonamides) showed a melting temperature range of 150-300°C, as determined by DTA, differential thermal analysis. Low melt temperatures, amorphism and high solubility behaviour of poly(amide-sulfonamides) can be attributed to the presence of non-ordered structures having a head-to-tail and head-to-head linkages.

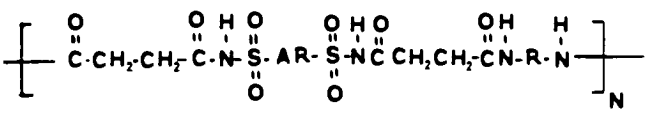
(CO-R-SO-NH-R'-NH-SO-R-CO-NH-R'-NH) (CO-R-SO-NH-R'NH-)

Head-to-Head Head-to-Tail

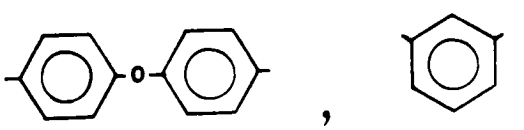
Poly(amide-sulfonamides) were also determined to be less thermally stable than the aromatic polyamides due to the presence of the sulfonamide group, despite the rigidity imposed by the aromatic rings in the main polymer chain (23).

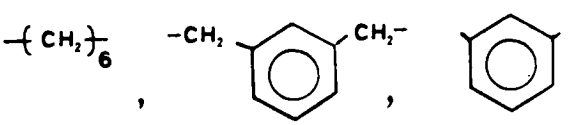
Another type of polymer worth describing is the polyacylsulfonamide-amides 13 . This class of polymer can be prepared by a ring opening reaction of N,N'-arylene disulfonyl bis(succinimides) with various diamines (24).

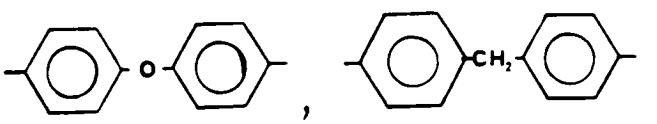




13

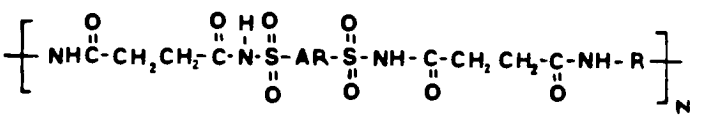
AR = 

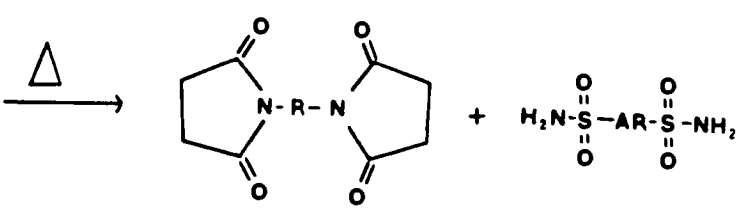
R = 



Solution polymerizations were carried out using polar solvents such as N-methyl-2-pyrrolidone and N,N-dimethylacetamide. The polymers obtained showed inherent viscosities ranging from 0.18-0.40 dL/g. These polymers were soluble in polar aprotic solvents such as N,N-dimethylacetamide, as well as in basic media such as sodium hydroxide and pyridine. It is interesting to note that these polymers were also soluble in acidic media such as formic acid and m-cresol, despite having the acidic sulfonamide linkages (24).

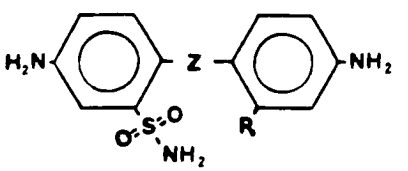
Differential thermal analysis of 13 showed a melting temperature in the range of 150-200°C. Thermal gravimetric analysis showed these polymers to have an initial % weight loss at around 200°C. It is believed that polyacylsulfonamide-amide 13 decomposes by the formation of bis-succinimides and the aromatic disulfonamides i.e.





This type of decomposition was supported by the appearance of the characteristic absorptions at $\bar{\nu}$= 1770 cm and $\bar{\nu}$= 1700 cm^{-1} assignable to the imide carbonyl in the infrared spectra of the decomposition residue of all of the polymers at 300°C under nitogen (24).

Poly(amide-sulfonamides) membranes are known to exhibit reverse osmosis properties. Due to the commercial value of these polymers, they usually are patented and synthetic details are never fully disclosed. A poly(amide-sulfonamides) reverse osmosis material was prepared by the polymerization of an aromatic diamine 14 with isophthaloyl chloride or adipoyl chloride (25).



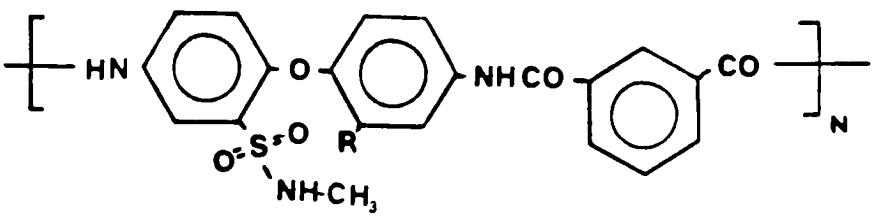
Z = CH_2 , O , SO_2 , S

R = SO_2NH_2 , H

14

The polymer was determined to have a tensile strength of 15kg/mm^2 and a 10% elongation at break. The polymer was cast from N,N-dimethylacetamide to give a 50μ film. The film was stable in air at $\lesssim$ 400°C. As a desalinating membrane, it showed a water permeation rate of 1.7 m^3/m^2/day and a salt rejection of 65% for water containing 5000 ppm sodium chloride.

Improvements in the membrane flux rate and % salt rejection were obtained when the sulfonamide substituents in diamine 14 were N-methylated (26).



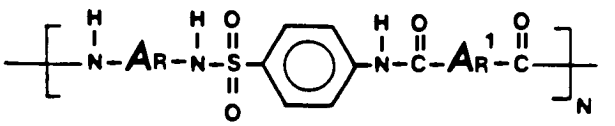
15

R = SO_2NHCH_3

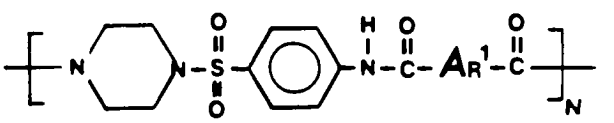
A solution of 2,2'-bis(methyl-aminosulfonyl) 4,4'-diamino-diphenyl-ether-isophthaloyl-chloride co-polymer 15 , having a reduced viscosity of 2.0 dL/g in N,N-dimethylacetamide at 30°C, was cast and gelled in ice water to give a membrane having a water flux rate of 1.3 $m^3/m^2/day$ and 88% salt rejection for water containing 5000 ppm sodium chloride. In comparision a cellulose acetate membrane showed 0.3 $m^3/m^2/day$ water flux rate and a 97% salt rejection for water containing 5000 ppm sodium chloride.

2.0 Objective.

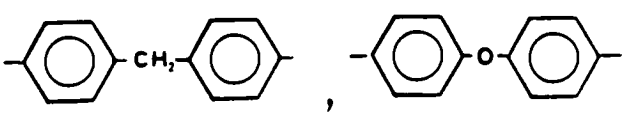
The aim of this research project was to synthesize and characterize several novel poly(amide-sulfonamides) having the general structure 16A and 16B shown below. These polymers are unique in structure from those previously synthesized and are potential candidates for reverse osmosis membranes.

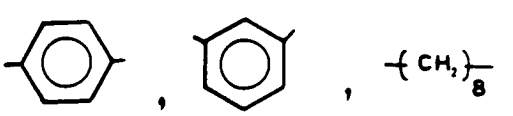


16A



16B

A_R = 

A_R^1 = 

Once synthesized, these polymers would be characterized by dilute solution viscosity, infrared spectroscopy, thermal gravimetric analysis and differential scanning calorimetry. In addition, films of these materials would be evaluated for mechanical and reverse osmosis properties.

3.0 Results and Discussion.

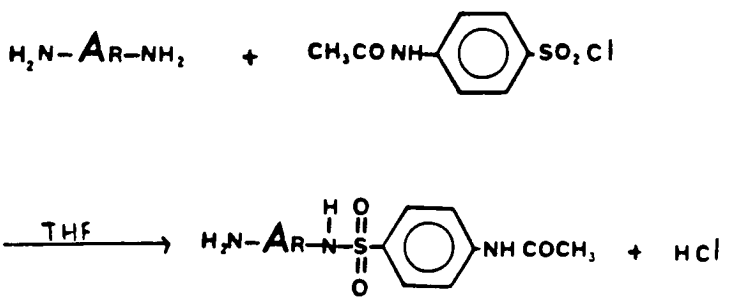
The synthesis of the title polymers involved;

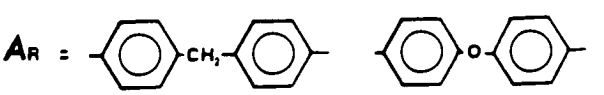
(1) synthesis of an amino acetanilide containing a a preformed sulfonamide linkage,

(2) deblocking of the amino acetanilide to form the diamine monomers,

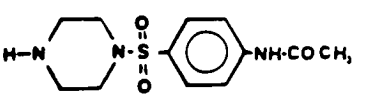
(3) solution polymerization of the diamine monomers with the appropriate dicarboxylic acid or derivative to form the poly(amide-sulfonamides).

The amino acetanilides 17-19 were prepared by reacting N-acetamidobenzene sulfonyl chloride with excess 4,4'-oxy dianiline, 4,4'-methylene dianiline and anhydrous piperazine in refluxing tetrahydrofuran.





17 , 18

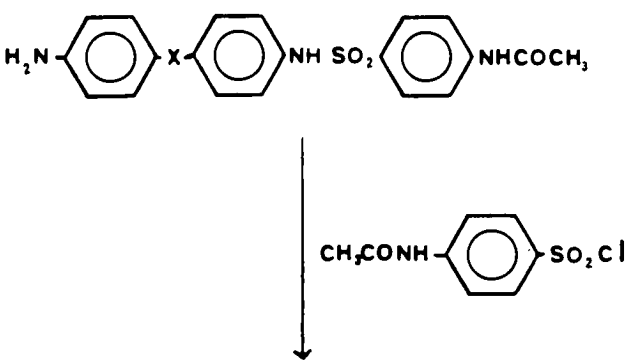


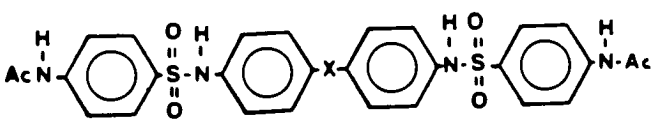
19

A 1 to 2 molar ratio of the N-acetamidobenzene sulfonyl chloride to the diamine was used to reduce the formation of an unwanted diacetanilide product 20 , a 2:1 adduct. The diacetanilide is formed because products 17-19 have a free amino group capable of reacting with a second molecule of N-acetamidobenzene sulfonyl chloride. These diacetanilides and their corresponding dianilines have been synthesized and used in the preparation of novel poly(amide-sulfonamides) (27).

The sulfonyl chloride was added dropwise to a vigorously stirred refluxing solution of the diamine in tetrahydrofuran for a period of two hours. Thin layer chromatography (ethyl acetate / hexane/ acetone 2:1:1) of the reaction mixture for the 4,4'-oxy and methylene dianiline always showed the presence of the diacetanilide product (slowest moving component) and the unreacted diamine. Since no acid acceptor was used in this reaction, the hydrogen chloride liberated was picked up by the excess starting diamine and the mono-acetanilide product. Evidence for this was the fact that the precipitate formed after the completion of the reaction was found to be soluble in water.

Thin layer chromatography analysis of the ethyl acetate extract of this solution showed it to consist of mainly starting diamine and a trace of the mono-acetanilide product. The individual components in the reaction mixture were separated using dry column chromatography. The yields of the pure mono-acetanilide 17-19 were low. These low yields can be attribute to the formation of the diacetanide product 20 , despite the care that was taken to avoid its formation.





20

X = $-CH_2-$, $-O-$

The NMR spectrum of 17 showed the methylene protons at δ= 3.7 ppm and the acetyl protons at δ= 2.1 ppm. The spectrum for 19 showed a singlet (8H) at δ= 2.5 ppm corresponding to the protons in the piperazine ring. The acetyl protons were also observed at δ= 1.8 ppm. The microanalysis of 17 gave a result which favourably corresponded to its structural composition.

The infrared spectra of 17,18,19 showed the characteristic N-H absorptions at ν= 3350, 3220, 3290 cm^{-1} for 17 , 18 and 19 , respectively. Table V summarizes the results of this selective sulfonylation reaction.

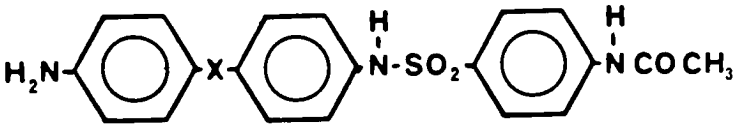
Table V: Results of the Selective Sulfonylation Reaction of 4,4'-Oxy Dianiline, 4,4'-Methylene Dianiline and Anhydrous Piperazine.

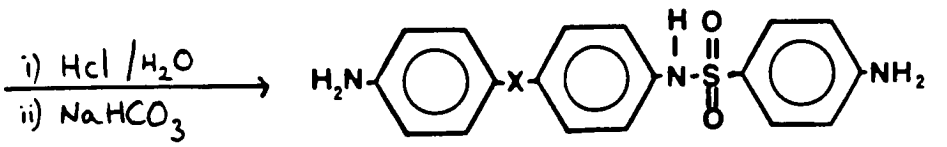
Compound	Melting Point(°C)	% Yield	Rf[a]		Microanalysis % C	H	N	S
17	175-176	48	0.59	cal	63.79	5.31	10.63	8.10
				fd.	63.51	5.35	10.32	7.98
18	146-147	46	0.60					
19	144-145	63	0.58[b]					

a) ethyl acetate/hexane/acetone (2:1:1) as the mobile phase.

b) diethyl ether/methanol (3:1) as the mobile phase.

The acetyl group in 17 , 18 and 19 was removed by treatment with 6 M hydrochloric acid under reflux condition for thirty minutes. This hydrolysis reaction gave the desired diamine monomers 21 , 22 and 23 in a fairly good yield.

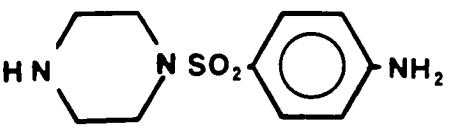




21 X = $-CH_2-$

22 X = $-O-$

23



The NMR spectra of 21 , 22 and 23 showed the disappearance of the acetyl protons at δ= 2.1 , δ= 2.2 ppm and δ=1.8 ppm, respectively. The diamine monomers 21 , 22 and 23 , all gave favourable microanalytical results and a single spot on thin layer chromatography.

The infrared spectra of the diamines 21 , 22 and 23 showed the absence of a carbonyl absorption band at ν= 1690 cm^{-1}, ν= 1680 cm^{-1} and ν= 1680 cm^{-1} respectively, indicating a successful deblocking reaction. The diamine monomers 21 and 22 showed a yellow colouration, even after treatment with decolourizing charcoal and column chromatography. Diamine monomer 23 was a white crystalline solid.

The results of the hydrolysis reaction are summarized in Table VI.

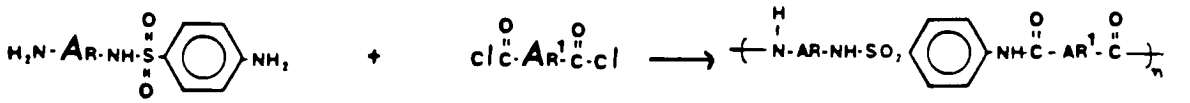
Table VI: Results of the Hydrolysis Reaction of the Mono Acetanilide 17 , 18 and 19 with 6 M Hydrochloric Acid.

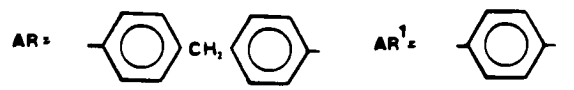
Compound	Melting Point(°C)	% Yield	Rf [a]		Microanalysis C	H	N	S
21	164-165	74	0.86	cal	64.58	5.38	11.89	9.06
				fd.	64.53	5.43	12.07	8.95
22	104-105	76	0.80	cal	60.84	4.78	11.83	9.01
				fd.	60.57	4.63	11.54	9.29
23	202-203	71	0.59 [b]	cal	49.79	6.22	17.42	13.27
				fd.	49.48	6.50	17.72	13.51

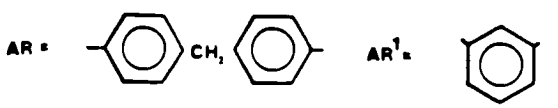
a) ethyl acetate/ hexane/ acetone (2:1:1) as the mobile phase.

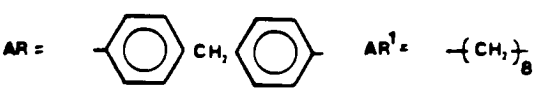
b) diethyl ether/ methanol (3:1) as the mobile phase.

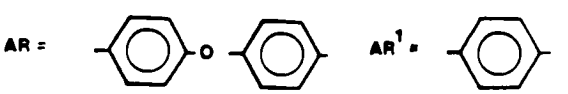
The diamine monomers 21 , 22 and 23 , purified by column chromatography, were reacted with terephthaloyl chloride, isophthaloyl chloride and sebacoyl chloride, using a low temperature solution polymerization technique to give the poly(amide-sulfonamides) 24-32.

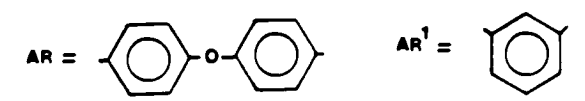


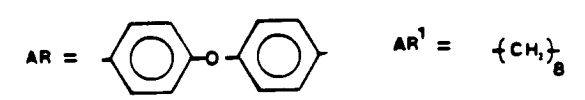
24 

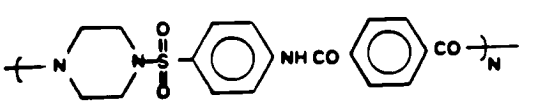
25 

26 

27 

28 

29 

30 

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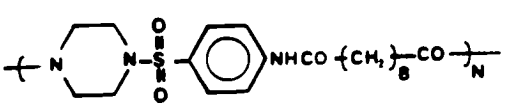
32 

The reactions of 21 with terephthaloyl, isophthaloyl and sebacoyl chloride were conducted at room temperature, to give polymers 24 , 25 and 26 . The polymers obtained had a very low inherent viscosities , indicative that they were low in molecular weight. A higher inherent viscosity of 0.49 dL/g was obtained for 24 when the reaction temperature was kept at 0-3 °C. Polymers 27 , 28 and 29 had the inherent viscosities of 0.31 , 0.31 and 0.49 dL/g respectively.

The low inherent viscosity values obtained were atteibuted to incomplete dryning of the diamine monomers and solvent. Repeating the experiment using monomer 21, dried over phosphorus pentoxide and refluxing toluene in a drying pistol under vacuum, gave polymers 24 , 25 and 26 which still had low inherent viscosity values.

The results of the polymerization of 21 , 22 and 23 with terephthaloyl, isophthaloyl and sebacoyl chloride using a low temperature solution polymerization technique are summarized in Table VII.

Table VII: Results of the Polymerization of 21 , 22 and 23 with Terephthaloyl, Isophthaloyl and Sebacoyl Chloride Using Low Temperature Solution Technique.

Polymer	Reaction Temp.(°C)	Inherent Viscosity (dL/g) [a]	% Yield	Tg (°C)	% Weight Loss at 300°C
(MBST) 24	21-23	0.25	91	243	5
(MBST) 24*	0-3	0.49	83	260	20
(MBSI) 25	21-23	0.19	70	220	7
(MBSS) 26	21-23	0.30	88	87	6
(OBST) 27	0-3	0.31	83	253	12
(OBSI) 28	0-3	0.31	70	256	12
(OBSS) 29*	0-3	0.49	82	142	14
(PBSS) 32	0-3	0.20	75	94	6.5

a) measured in N,N-dimethylacetamide at 25°C with the concentration = 0.50g/100ml.

* Film forming polymers.

The polymers 24-29 , synthesized using the low temperature solution technique showed a decomposition in structure at 300- 360°C in a nitrogen atmosphere.

In one polymerization, 2,6-dimethyl pyridine was used instead of pyridine as the acid acceptor. An example of this was the polymerization of 23 with sebacoyl chloride to give polymer 32 . Using a 1-ml syringe, sebacoyl chloride was injected into a stirred diamine solution to give a precipitate of polymer 32 almost instantaneously. Polymer 32 , having a highly flexible aliphatic chain in the polymer structure showed a 6.5 % weight loss at 300°C . The glass transition temperature was also found to be at 94°C. Polymer 32 had an inherent viscosity of 0.20 dL/g,suggesting a low in molecular weight material.

Since the inherent viscosity values for the polymers prepared by a low temperature solution technique were low, a new polymerization technique was employed in order to achieve higher inherent viscosities.

Higher molecular weight polymers were obtained when the Yamazaki reaction was used (13). When 22 was treated with isophthalic acid, a polymer 28 , having an inherent

viscosity of 1.21 dL/g was obtained. The reaction of 21 with terephthalic and isophthalic acid gave polymers 24 and 25 with moderate inherent viscosities values of 0.38- 0.50 dL/g. The low inherent viscosity values for polymers 24 and 25 were attributed to incomplete dryness of the monomers.

Polymer 27 showed an inherent viscosity of 0.45 dL/g. However, polymers 24 , 25 and 27 , despite their low inherent viscosities values, formed tough transparent films when cast from N,N-dimethylacetamide solution.

Polymers 30 and 31 prepared from the piperazine-benzene-sulfonamido monomer 23 and terephthalic, isophthalic acid, showed low inherent viscosities values of 0.20- 0.22 dL/g. These polymers formed brittle films when cast from N,N-dimethylacetamide solution.

The results of these Yamazaki polymerizations are summarized in Table VIII.

Table VIII: Results of the Polymerization of 21 , 22 and 23 with Terephthalic, Isophthalic Acid using the Yamazaki Reaction.

Polymer	%Yield	Inherent Viscosity (dL/g)[a]	Tg(°C)	% Weight Loss at 300°C
(MBST) 24*	99	0.50	260	20
(MBSI) 25*	100	0.38	198	19
(OBST) 27*	100	0.45	273	20
(OBSI) 28*	96	1.21	268	18
(PBST) 30	81	0.22	200	9
(PBSI) 31	74	0.21	273	8
(OBSP) 33	93	0.22	238	16.5

a) measured in N,N-dimethylacetamide at 25°C with the concentration = 0.500g/100 mL.

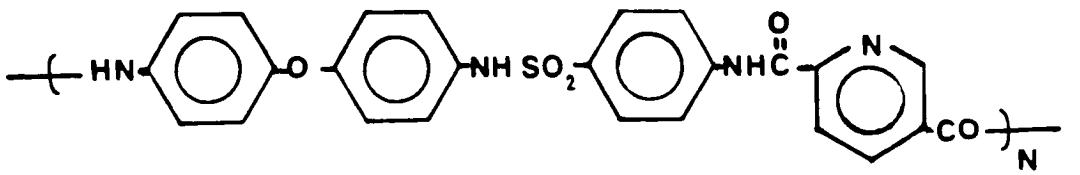
* Film forming polymers.

One advantage the Yamazaki reaction has over the low temperature solution polymerization is the utilization of a dicarboxylic acid instead of the diacid chloride. The step growth polymerization process requires high monomers purity in order to form a high molecular weight material. Since the diacid chloride are very reactive, they can react with water in the atmosphere to form a dicarboxylic acid which terminates the step growth polymerization process leading to lower molecular weight polymers.

The dryness and purity of the diamine monomers, the dicarboxylic acid and the solvent used are important factors in the Yamazaki reaction. All of the diamines monomers used in this project contained a preformed sulfonamide group, which can strongly associate with water or solvents used by hydrogen bonding. Despite the fact that all of the diamine monomers gave favourable microanalyses and showed a single spot on the thin layer chromatography, it was necessary to purify the monomers using dry column chromatography and recrystallization.

Recrystallization of monomer 22 twice, gave a white crystalline product. This monomer when reacted with isophthalic acid gave a high molecular weight polymer having an inherent viscosity of 1.21 dL/g.

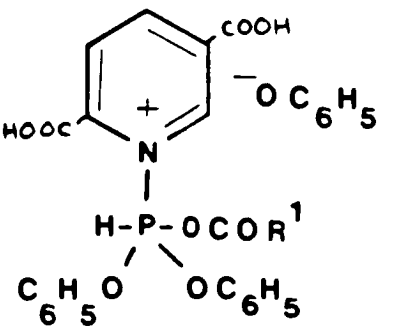
Another interesting polymer was synthesized by reacting 22 with 2,5-pyridine dicarboxylic acid to form poly(imino-1,4-phenylenesulfonylimino-1,4-phenylene-oxy-1,4-phenyleneiminocarbonyl-2,5-pyridinediylcarbonyl) 33.



33

Polymer 33 had an inherent viscosity value of 0.22 dL/g and a glass transition temperature of 238°C. A film cast from N,N-dimethylacetamide polymer solution was brittle. Since the Yamazaki reaction technique was used, it is believed that some of the 2,5-pyridine dicarboxylic acid may have reacted to form a nitrogen-phosphorus linkage in the triphenyl phosphite complex 34 .

The formation of this complex would reduce the amount of the dicarboxylic acid available for the polymerization process.



34

Having obtained a low inherent viscosity for 33 , the reaction of 2,5-pyridine dicarboxylic acid with other diamine monomers was not further investigated.

All of the polymers 24-33 were found to be soluble in N,N-dimethylacetamide, N-methyl-2-pyrrolidone and concentrated sulfuric acid. Some of the polymers were also found to be partially soluble in a 10% sodium hydroxide solution. The solubility test results are summarized in Table IX.

From the results presented in this report, it can be concluded that it is possible to prepare high molecular weight polymers containing a sulfonamide groups in the polymer backbone. Lack of time and monomers, prevented a large scale preparation of polymers 26, 29 and 32 .

The mechanical and reverse osmosis properties of polymer 24 , 25 , 27 and 28 are currently under investigation.

a

Table IX: Solubility of Poly(amide-sulfonamides) in Various Organic Solvents.

Solvent	Polymer									
	24	25	26	27	28	29	30	31	32	33
N,N-dimethylacetamide	+	+	+	+	+	+	+	+	+	+
N-methyl-2-pyrrolidone	+	+	+	+	+	+	+	+	+	+
N,N-dimethylformamide	+	+	+	+	+	+	+	+	+	+
conc. sulfuric acid	+	+	+	+	+	+	+	+	+	+
Pyridine	+	+	+	+	+	+	±	±	±	±
10% sodium hydroxide	±	±	±	±	±	±	-	-	-	-
2-methoxy ethyl ether	±	±	±	±	±	±	-	-	±	±
tetrahydrofuran	±	+	±	±	±	±	-	-	±	±
acetone	-	±	±	-	±	±	-	-	±	±
chloroform	-	-	±	-	-	±	-	-	±	-
95% ethanol	-	-	-	-	-	-	-	-	-	-
ethyl acetate	-	-	-	-	-	-	-	-	-	-

+ = soluble

± = partially soluble or swelling

- = insoluble

a) determined at 25°C

4.0 Experimental

General information

1) Pyridine and N-methyl-2-pyrrolidone were distilled under reduced pressure and stored under nitrogen.

2) All melting points were determined in capillaries using a Mel-temp apparatus and are uncorrected.

3) ^1H NMR spectra were determined using a Hitachi Perkin Elmer R-20 operating at 60 MHz with teramethylsilane as the internal standard.

4) Unless otherwise stated, infrared spectra of all samples were done as potassium bromide pellets or films using a Perkin-Elmer PE-681 infrared spectrophotometer.

5) Dry column chromatography were done using Kieselgel 60 F254 as the stationary phase.

6) Microanalyses were determined by the Analytical Division of the Baron Consulting Company, Orange, Connecticut 06477.

7) All concentration processes were done by using a Büchi rotary evaporator with the temperature not exceeding 60°C.

8) Terephthaloyl and isophthaloyl chloride were recrystallized from n-hexane.

9) Terephthalic acid ,isophthalic acid, 4,4'-oxy dianiline and 4,4'methylene dianiline were obtained from Aldrich Chemical Co.; anhydrous piperazine and triphenylphosphite were obtained from Eastman-Kodak Co. and were used as such.

10) N,N-dimethylacetamide spectrograde 99+% was obtained from Aldrich Chemical Co. and was used as such.

11) Thermal gravimetric analyses of all polymers were determined by using a Perkin-Elmer TGS-2 thermal analysis under a nitrogen atmosphere with the heating rate being 20°C per minute.

12) Differential Scanning Calorimetry analyses were determined using a Perkin-Elmer DSC-4.
A heating rate of 10-20°C per minute and a range of 0.5-2.0 mcal per second was used.

13) Thin Layer Chromatography analyses were carried out on Eastman Chromagram sheets (13181 silica gel).

14) Inherent viscosities were determined using a Canon viscometer no.1 C426 at a constant temperature of 25°C, the polymers concentration was 0.50g in 100 ml N,N-dimethylacetamide.

15) Solubility tests were performed qualitatively at 25°C.

Synthesis of N-acetylimino-1,4-phenylenesulfonylimino-1,4-phenylenemethylene-1,4-phenyleneamine 17.

In a 5000 ml three necked round bottom flask fitted with a Friedrich condenser and a mechanical stirrer, 90 g (0.45 mole) of 4,4'-methylene dianiline was dissolved in 2500 ml tetrahydrofuran. The solution was stirred under reflux for thirty minutes. To this solution was added dropwise from a pressure equalizing funnel, 53.06 g (0.22 mole) of N-acetamidobenzene sulfonyl chloride in 500 ml tetrahydrofuran. The mixture was stirred under reflux for five hours. The solution mixture was cooled and the precipitate filtered. Evaporation of the filtrate gave a brown viscous syrup which was chromatographed using hexane/ ethyl acetate/ acetone (3:2:1) as the eluting solvent. This gave brown crystals of 17 with Rf = 0.59 (ethyl acetate/hexane/ acetone 2:1:1). The product was dried overnight in a vacuum oven at 70°C and was used as such for further transformation.

yield = 43 g (48%)

m.p. = 175-176°C

Analytical for $C_{21}H_{20}N_3SO_3$

calculated: C= 63.79% H= 5.31% N= 10.63% S= 8.10%

found : C= 63.51% H= 5.35% N= 10.32% S= 7.98%

IR data (KBr): ν = 3350 cm^{-1} (N-H), ν = 1685 cm^{-1} (C=O), ν = 1150 cm^{-1} (S=O)

Synthesis of N-acetylimino-1,4-phenylenesulfonylimino-1,4-phenylene-oxy-1,4-phenyleneamine 18.

Using the procedure previously described in the synthesis of 17, 150 g (0.750 mole) of 4,4'-oxy dianiline in 2500 ml tetrahydrofuran was reacted with 87.56 (0.37 mole) of N-acetamidobenzene sulfonyl chloride in 500 ml tetrahydrofuran.

yield = 69.60 g (46%)

m.p. = 146-147°C

Rf = 0.60 (ethyl acetate/ hexane/acetone 2:1:1)

IR data (KBr): ν = 3220 cm^{-1} (N-H)

ν = 1680 cm^{-1} (C=O)

ν = 1160 cm^{-1} (S=O)

This product was dried overnight in a vacuum oven at 70°C and was used as such for further transformation.

Synthesis of N-acetylimino-1,4-phenylenesulfonylpiperizinyl. 19

Using the same procedure for the synthesis of 17 and 18 , 100g (1.16 mole) of anhydrous piperazine in 1500 ml tetrahydrofuran was reacted with 135.63g (0.58 mole) of N-acetamidobenzene sulfonyl chloride in 500ml tetrahydrofuran for five hours. Filtration of the precipitate and evaporation of the excess solvent gave white crystalline solid. The solid was redissolved in methanol and was chromatographed using diethyl ether/ methanol (4:1) as the eluting solvent. This gave pale yellow crystalline solid of 19 with the Rf = 0.61 (diethyl ether/ methanol 3:1). The product was dried overnight in a vacuum oven at 70°C and was used as such.

yield = 105.2 g (63%)

m.p.= 144-145°C

IR data (KBr): ν= 3280 cm^{-1} (N-H)

ν= 1680 cm^{-1} (C=O)

ν= 1170 cm^{-1} (S=O)

Synthesis of Amino-1,4-phenylenesulfonylimino-1,4-phenylenemethylene-1,4-phenyleneamine 21.

Using a 500 ml round bottom flask fitted with a condenser and a magnetic stirrer, 9 g(0.02 mole) of 17 was treated with 100 ml 6M hydrochloric acid. The mixture was refluxed for thirty minutes. The mixture was cooled in an ice water bath and was neutralized by the careful additions of sodium bicarbonate to gave a yellow precipitate of 21 , which was dried overnight in a vacuum oven at 70°C.

yield = 5.98 g (74%)

This crude product was dissolved in acetone and was chromatographed using hexane/ ethyl acetate/ acetone (3:2:1) as the eluting solvent. This gave pale yellow crystals of 21 . The product was further purified by recrystallization from methanol. The recrytallized product was dried overnight in a vacuum oven at 70°C. It was further dried in a pistol over phosphorus pentoxide and refluxing cyclohexane for twelve hours.

m.p. = 164 - 165°C

Analytical for $C_{19} H_{19} N_3 O_2 S$

calculated: C= 64.58% H= 5.38% N= 11.89% S= 9.06%

found: C= 64.53% H= 5.43% N= 12.07% S= 8.95%

IR data (KBr): ν= 3400 cm^{-1} (N-H), ν= 1140 cm^{-1} (S=O)

Synthesis of Amino-1,4-phenylenesulfonylimino-1,4-phenyleneoxy-1,4-phenyleneamine 22.

Using the same procedure previously described, 30 g (0.07 mole) of 18 was treated with 200 ml 6M hydrochloric acid for thirty minutes. The cooled solution was neutralized with sodium bicarbonate to give the crude solid diamine product 22.

yield = 20.38 g (76%)

This crude product was dissolved in acetone and chromatographed using ethyl acetate/ hexane/ acetone (3:2:1) as the eluting solvent to give a brown syrup of 22 . The syrup was redissolved in a minimum amount of ethanol (c.a. 100 ml). Adding 30 ml cold distilled water to this solution and storing it overnight at minus 25°C, gave pale yellow needles of 22 . This product was dried in the same manner as 21 .

m.p. = 104- 105°C

Analytical for $C_{18} H_{17} N_3 O_3 S$

cal. :C= 60.84% H= 4.78% N= 11.83% S= 9.01%

found:C= 60.57% H= 4.63% N= 11.54% S= 9.29%

IR data (KBr): ν = 3260 cm^{-1} (N-H)

ν = 1155 cm^{-1} (S=O)

Synthesis of Amino-1,4-phenylenesulfonylpiperizinyl. 23

Using the same procedure as that of 21 and 22 , 30 g (0.10 mole) of 19 was treated with 200 ml of 6 M hydrochloric acid for fifteen minutes. The solution was cooled in an ice water bath and neutralized with sodium bicarbonate to give a yellow precipitate. The precipitate was filtered and dried overnight at 70°C in a vacuum oven.

yield = 17.82 g (71%)

This crude product was recrystallized from methanol to give white crystals of 23 , which was dried for an overnight period in a vacuum oven at 70°C. It was further dried in a drying pistol over phosphorous pentoxide and refluxing toluene for twelve hours.

m.p. = 202- 203°C

Analytical for $C_{10}H_{15}N_3O_2S$

cal. C= 49.79% H= 6.22% N= 17.42% S= 13.27%

found C= 49.48% H= 6.50% N= 17.72% S= 13.51%

IR data (KBr): ν = 3440 cm^{-1} (N-H)

ν = 1150 cm^{-1} (S=O)

This product was used as such for the polymerization process.

General low temperature solution polymerization procedure.

Using a 50-ml one necked round bottom flask, the diamine was dissolved in 10 ml of spectrophotometric grade N,N-dimethylacetamide containing 5 ml pyridine. The solution was stirred and chilled in an ice bath for thirty minutes. The acid chloride was added rapidly to the stirring mixture.

The mixture was left stirring at 0-3°C for six hours and overnight at 21-23°C.

The polymer was obtained by pouring the mixture into a beaker containing 200 ml cold distilled water. The polymer was filtered and dried in a vacuum oven at 90°C for an overnight period.

General Yamazaki polymerization procedure.

To a 300 ml three necked round bottom flask fitted with a thermometer, a condenser and a nitrogen inlet valve was added the diamine, terephthalic acid, 2 g lithium chloride, 10.6 ml triphenyl phosphite, 10 ml pyridine and 40 ml N-methyl-2-pyrrolidone. The mixture was heated with stirring at 85-90°C for 16 hours under nitrogen. When cooled, the reaction mixture was poured into a beaker containing 300 ml methanol. The precipitated polymer was collected by filtration and dried in a vacuum oven at 90°C for an overnight period.

Synthesis of poly(imino-1,4-phenylenesulfonylimino-1,4-phenylenemethylene-1,4-phenyleneiminoterephthaloyl) (MBST) 24.

Using the low temperature solution polymerization procedure, 0.50 g (1.41×10^{-3} mole) of 21 was reacted with 0.28 g (1.41×10^{-3} mole) of terephthaloyl chloride to produce polymer 24 .

yield = 0.66 g (83%)

$\eta_{inh.}$ = 0.49 dL/g

Tg = 260°C

IR data (film): ν = 3300 cm^{-1} (N-H)

ν = 1660 cm^{-1} (C=O)

ν = 1155 cm^{-1} (S=O)

PDT = 340°C

Synthesis of poly(imino-1,4-phenylenesulfonylimino-1,4-phenylenemethylene-1,4-phenyleneiminoisophthaloyl) (MBSI) 25.

Using the low temperature solution polymerization procedure, 0.50 g (1.41×10^{-3} mole) of 21 was reacted with 0.28 g (1.41×10^{-3} mole) of isophthaloyl chloride to give polymer 25 .

yield = 0.48 g (70%)

η_{inh} = 0.19 dL/g

Tg = 220 °C

PDT = 350°C

IR data (KBr): ν = 3300 cm^{-1} (N-H)

ν = 1655 cm^{-1} (C=O)

ν = 1155 cm^{-1} (S=O)

Synthesis of poly(imino-1,4-phenylenesulfonylimino-1,4-phenylenemethylene-1,4-phenyleneiminosebacoyl) (MBSS) 26.

Using the low temperature solution polymerization procedure, 0.50 g (1.41×10^{-3} mole) of 21 was reacted with 0.3 ml (1.41×10^{-3} mole) of sebacoyl chloride to give polymer 26 .

yield = 0.65 g (88%)

$\eta_{inh.}$ = 0.30 dL/g

Tg = 87°C

IR data (KBr): ν = 3340 cm^{-1} (N-H)

ν = 1660 cm^{-1} (C=O)

ν = 1150 cm^{-1} (S=O)

PDT = 310°C

Synthesis of poly(imino-1,4-phenylenesulfonylimino-1,4-phenylene-oxy-1,4-phenyleneiminoterephthaloyl) (OBST) 27.

Using the low temperature solution polymerization procedure, 0.50 g (1.41×10^{-3} mole) of 22 was reacted with 0.28 g (1.41×10^{-3} mole) of terephthaloyl chloride to give polymer 27.

yield = 0.56 g (83%)

$\eta_{inh.}$ = 0.31 dL/g

Tg = 253°C

IR data (KBr): ν = 3320 cm^{-1} (N-H)

ν = 1660 cm^{-1} (C=O)

ν = 1155 cm^{-1} (S=O)

PDT = 370°C

Synthesis of poly(imino-1,4-phenylenesulfonylimino-1,4-phenylene-oxy-1,4-phenyleneiminoisophthaloyl) (OBSI) 28.

Using the low temperature solution polymerization procedure, 0.50 g (1.41×10^{-3} mole) of 22 was reacted with 0.28 g of isophthaloyl chloride to give polymer 28.

yield = 0.48 g (70%)

$\eta_{inh.}$ = 0.31 dL/g

Tg = 256°C

IR data (KBr): ν = 3320 cm^{-1} (N-H)

ν = 1660 cm^{-1} (C=O)

ν = 1155 cm^{-1} (S=O)

PDT = 370°C

Synthesis of poly(imino-1,4-phenylenesulfonylimino-1,4-phenylene-oxy-1,4-phenyleneiminosebacoyl) (OBSS) 29.

Using the low temperature solution polymerization procedure, 0.50 g (1.41×10^{-3} mole) of 22 was reacted with 0.3 ml sebacoyl chloride to give polymer 29.

yield = 0.61 g (82%)

Tg = 142°C

$\eta_{inh.}$ = 0.49 dL/g

IR data (film): ν = 3250 cm^{-1} (N-H)

ν = 1660 cm^{-1} (C=O)

ν = 1155 cm^{-1} (S=O)

PDT = 340°C

Synthesis of poly(imino-1,4-phenylenesulfonyl-piperazinylenesebacoyl) (PBSS) 32.

Using a 25-ml one necked round bottom flask, 1.01 g (0.0042 mole) of 23 was dissolved in 20 ml N,N-dimethylacetamide and 5 ml 2,6-dimethyl pyridine. The solution mixture was stirred and chilled in an ice bath for thirty minutes. Using a 1-ml syringe, 0.9 ml (0.0042 mole) of sebacoyl chloride was injected to the stirred solution. The mixture was stirred at 0-3°C for six hours and then overnight at 21-24°C. The polymer was precipitated by pouring the solution mixture into 100 ml cold distilled water. The polymer was filtered, washed with 50 ml cold distilled water and dried in a vacuum oven at 50°C for overnight.

yield = 1.53 g (75%)

$\eta_{inh.}$ = 0.20 dL/g

Tg = 94°C

IR data (KBr): ν = 3380 cm^{-1} (N-H)

ν = 1700 cm^{-1} (C=O)

ν = 1160 cm^{-1} (S=O)

PDT = 340°C

Synthesis of poly(imino-1,4-phenylenesulfonylimino-1,4-phenylenemethylene-1,4-phenyleneiminoterephthaloyl) (MBST). 24

Using the general Yamazaki polymerization procedure, 3.53 g (0.01 mole) of 21 was reacted with 1.66 g terephthalic acid in 20 ml N-methyl-2-pyrrolidone, 5 ml pyridine, 5.3 ml triphenyl phosphite containing 1 g of lithium chloride to give polymer 24.

yield = 4.65 g (99%)

$\eta_{inh.}$ = 0.50 dL/g

Tg = 260°C

IR data (film): ν = 3300 cm^{-1} (N-H)

ν = 1660 cm^{-1} (C=O)

ν = 1155 cm^{-1} (S=O)

PDT = 340°C

Synthesis of poly(imino-1,4-phenylenesulfonylimino-1,4-phenylenemethylene-1,4-phenyleneiminoisophthaloyl) (MBSI). 25

Using the general Yamazaki polymerization procedure, 6.90 g (0.019 mole) of 21 was reacted with 3.24 g (0.019 mole) of isophthalic acid to give polymer 25.

yield = 12.14 g (100%)

$\eta_{inh.}$ = 0.38 dL/g

Tg = 198°C

IR data(film): ν = 3330 cm^{-1} (N-H)

ν = 1655 cm^{-1} (C=O)

ν = 1155 cm^{-1} (S=O)

PDT = 350°C

Synthesis of poly(imino-1,4-phenylenesulfonylimino-1,4-phenylene-oxy-1,4-phenyleneiminoterephthaloyl) (OBST). 27

Using the general Yamazaki polymerization procedure, 7.10 g (0.02 mole) of 22 was reacted with 3.32 g of terephthalic acid to give polymer 27.

yield = 12.62 g (100%)

$\eta_{inh.}$ = 0.45 dL/g

Tg = 273°C

IR data (film): ν = 3320 cm^{-1} (N-H)

ν = 1660 cm^{-1} (C=O)

ν = 1155 cm^{-1} (S=O)

PDT = 370°C

Synthesis of poly(imino-1,4-phenylenesulfonylimino-1,4-phenylene-oxy-1,4-phenyleneiminoisophthaloyl) (OBSI). 28

Using the general Yamazaki polymerization procedure, 7.10 g (0.02 mole) of 22 was reacted with 3.32 g (0.02 mole) isophthalic acid to give polymer 28.

yield = 11.90 g (96%)

$\eta_{inh.}$ = 1.21 dL/g

Tg = 268°C

IR data (film): ν = 3320 cm^{-1} (N-H)

ν = 1660 cm^{-1} (C=O)

ν = 1155 cm^{-1} (S=O)

PDT = 370°C

Synthesis of poly(imino-1,4-phenylenesulfonylimino-1,4-phenylene-oxy-1,4-phenyleneiminocarbonyl-2,5-pyridine-diylcarbonyl) (OBSP). 33

Using the general Yamazaki polymerization procedure, 7.10 g (0.02 mole) of 22 was reacted with 3.34 g (0.02 mole) of 2,5-pyridine dicarboxylic acid to give polymer 33.

yield = 11.57 g (93%)

$\eta_{inh.}$ = 0.22 dL/g

Tg = 238°C

IR data (KBr): ν = 3400 cm^{-1} (N-H)

ν = 1660 cm^{-1} (C=O)

ν = 1150 cm^{-1} (S=O)

PDT = 360°C

Synthesis of poly(imino-1,4-phenylenesulfonylpiperazinyleneterephthaloyl) (PBST). (30)

Using the general Yamazaki polymerization procedure, 4.82 g (0.02 mole) of 23 was reacted with 3.34 g (0.02 mole) of terephthalic acid to give polymer 30.

yield = 8.24 g (81%)

$\eta_{inh.}$ = 0.22 dL/g

Tg = 200°C

IR data (KBr): ν = 3450 cm^{-1} (N-H)

ν = 1660 cm^{-1} (C=O)

ν = 1160 cm^{-1} (S=O)

PDT = 375°C

Synthesis of poly(imino-1,4-phenylenesulfonylpiperazinyleneisophthaloyl) (PBSI). (31)

Using the general Yamazaki polymerization procedure, 4.82 g (0.02 mole) of 23 was reacted with 3.34 g (0.02 mole) of isophthalic acid to give polymer 31.

yield = 7.56 g (74%)

$\eta_{inh.}$ = 0.21 dL/g

Tg = 273°C

IR data (KBr): ν = 3440 cm^{-1} (N-H)

ν = 1680 cm^{-1} (C=O)

ν = 1160 cm^{-1} (S=O)

PDT = 370°C

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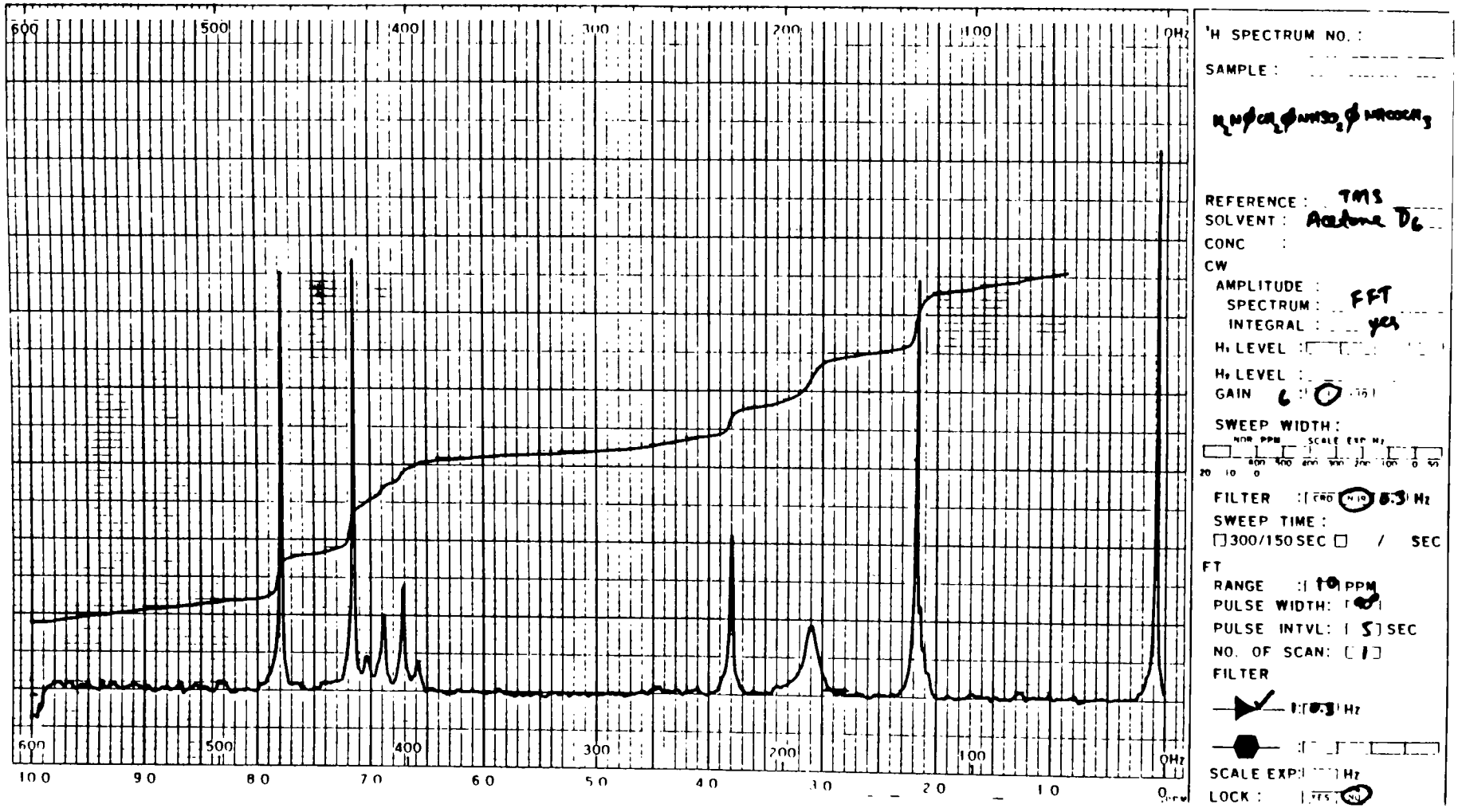


Figure 1: ^{1}H NMR spectrum of N-acetylimino-1,4-phenylene-sulfonylimino-1,4-phenylenemethylene-1,4-phenyleneamine. 17

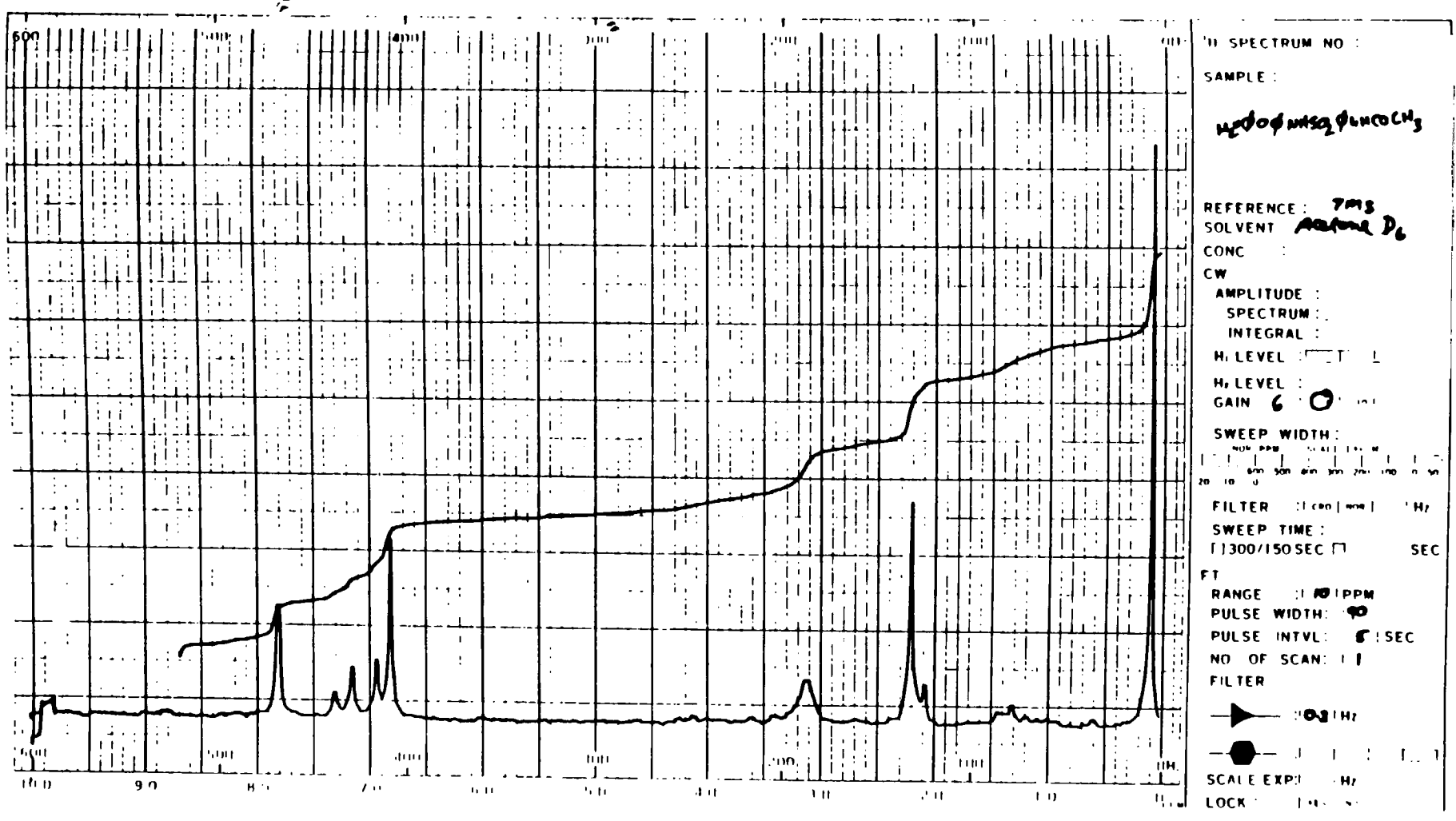


Figure 2: ^{1}H NMR spectrum of N-acetylimino-1,4-phenylene-sulfonylimino-1,4-phenylene-oxy-1,4-phenylene-amine. 18

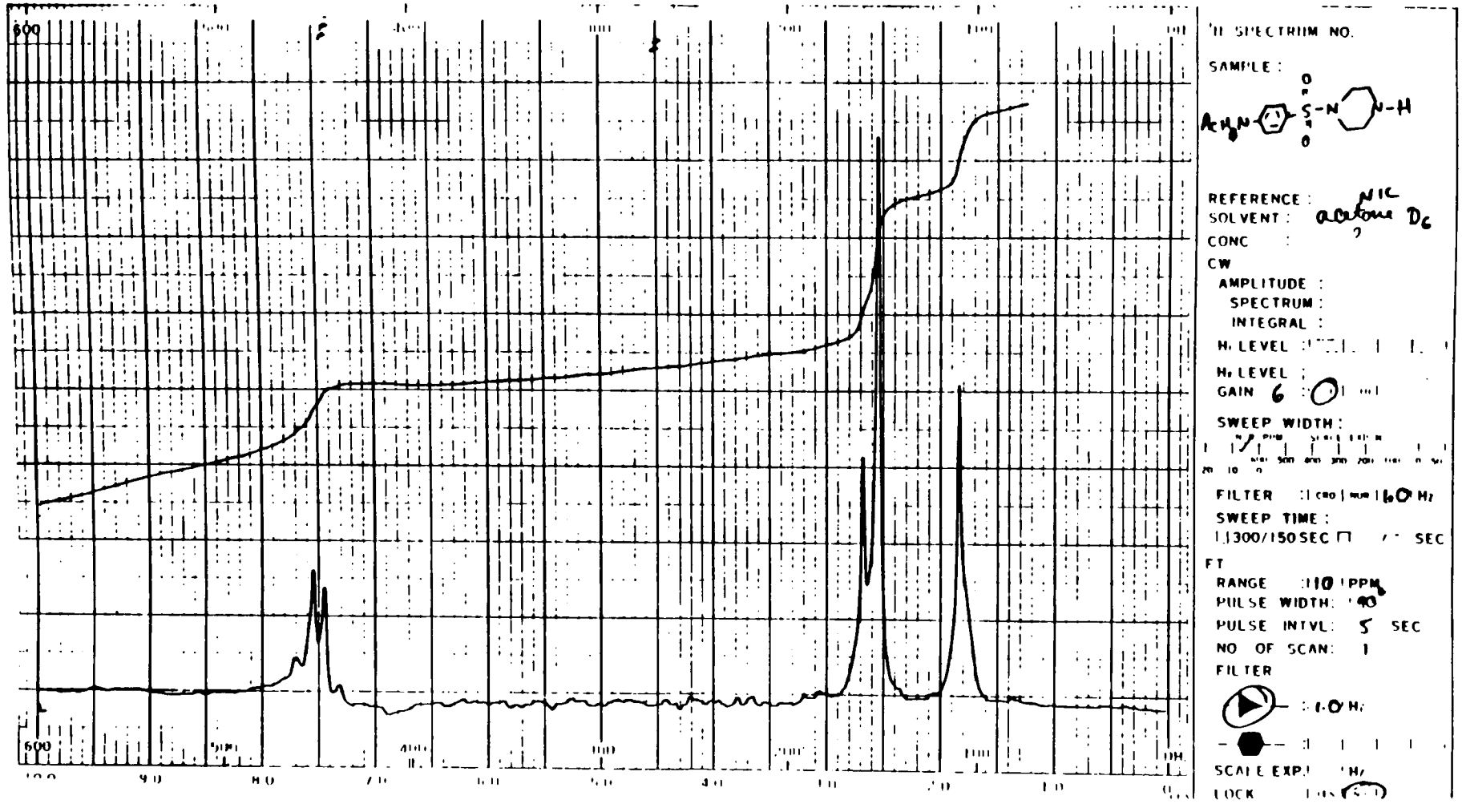


Figure 3: ^{1}H NMR spectrum of N-acetylimino-1,4-phenylene-sulfonylpiperizinyl. 19

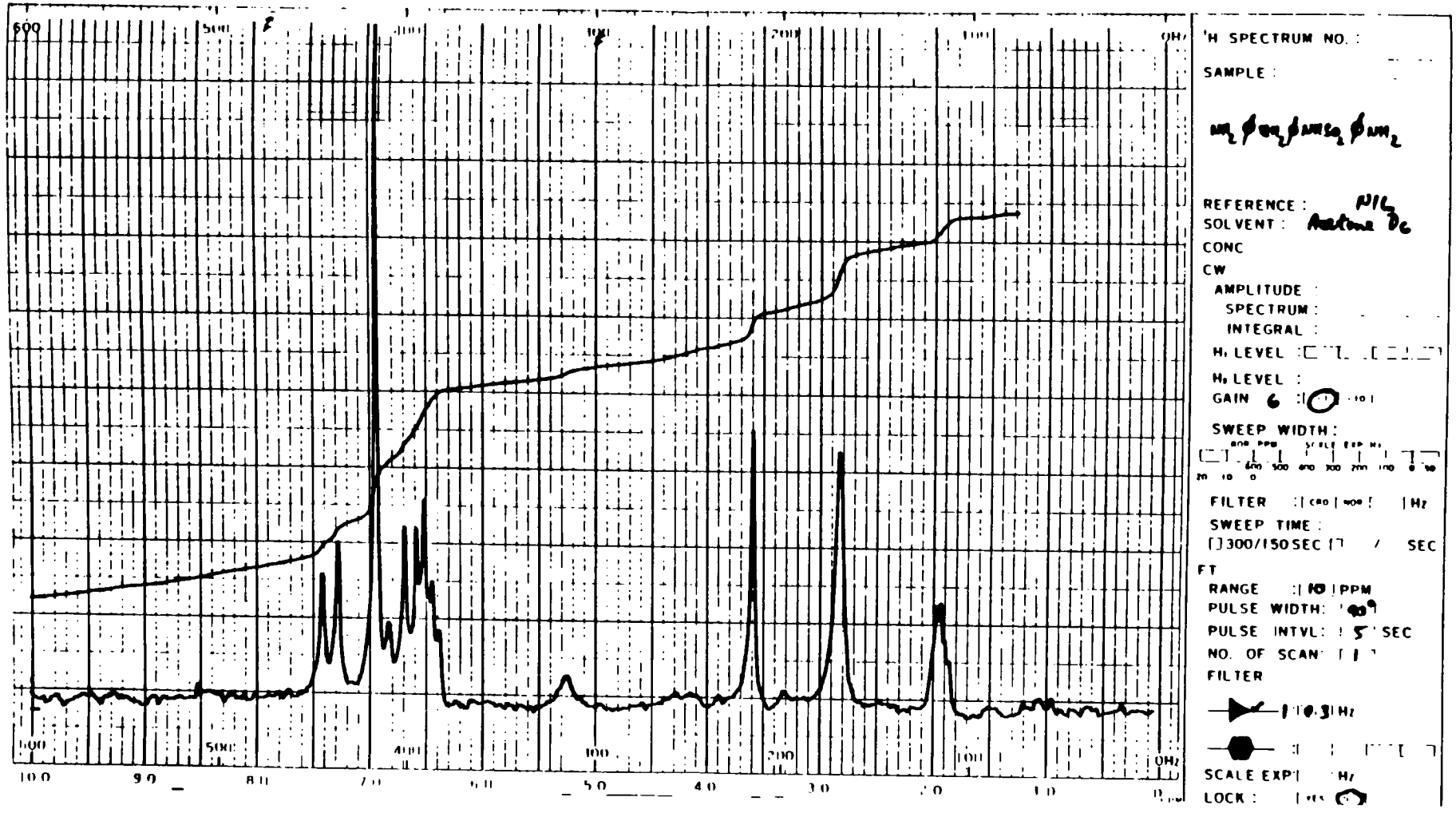


Figure 4: ^{1}H NMR spectrum of Amino-1,4-phenylenesulfonylimino-1,4-phenylenemethylene-1,4-phenyleneamine. 21

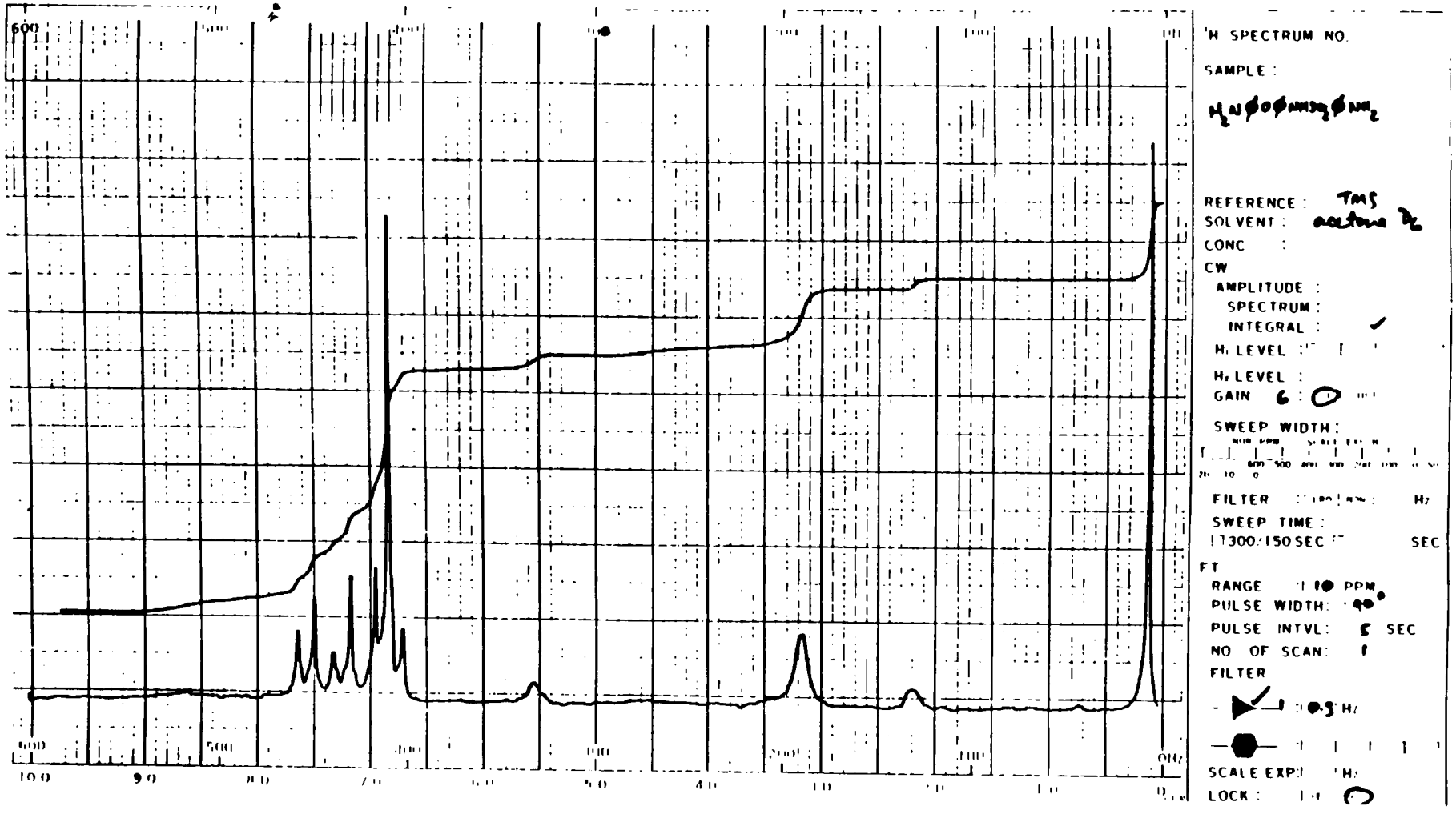


Figure 5: ^{1}H NMR spectrum of Amino-1,4-phenylenesulfonylimino-1,4-phenylene-oxy-1,4-phenyleneamine. 22

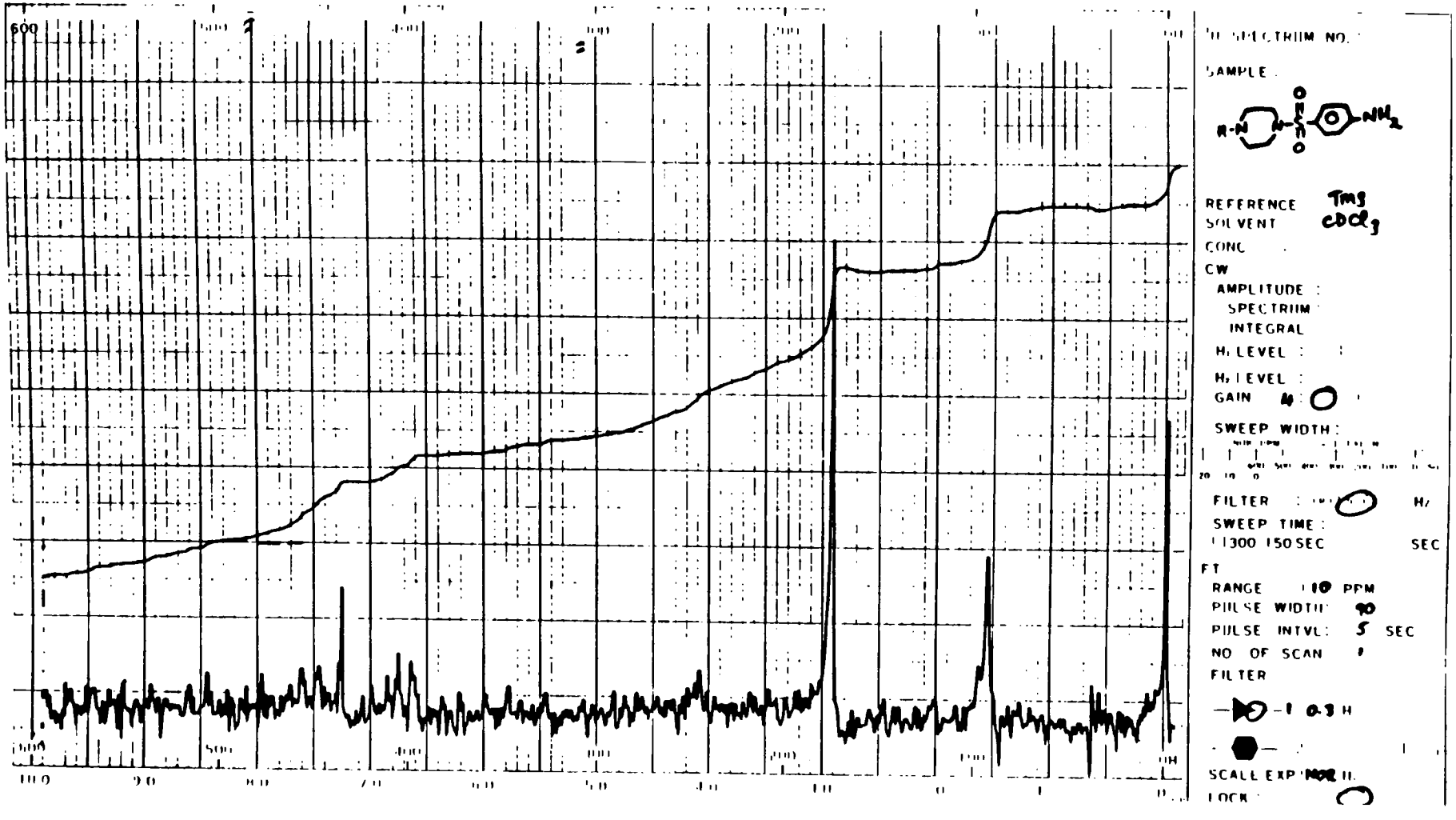


Figure 6: ^{1}H NMR spectrum of Amino-1,4-phenylenesulfonyl-piperizinyl. 23

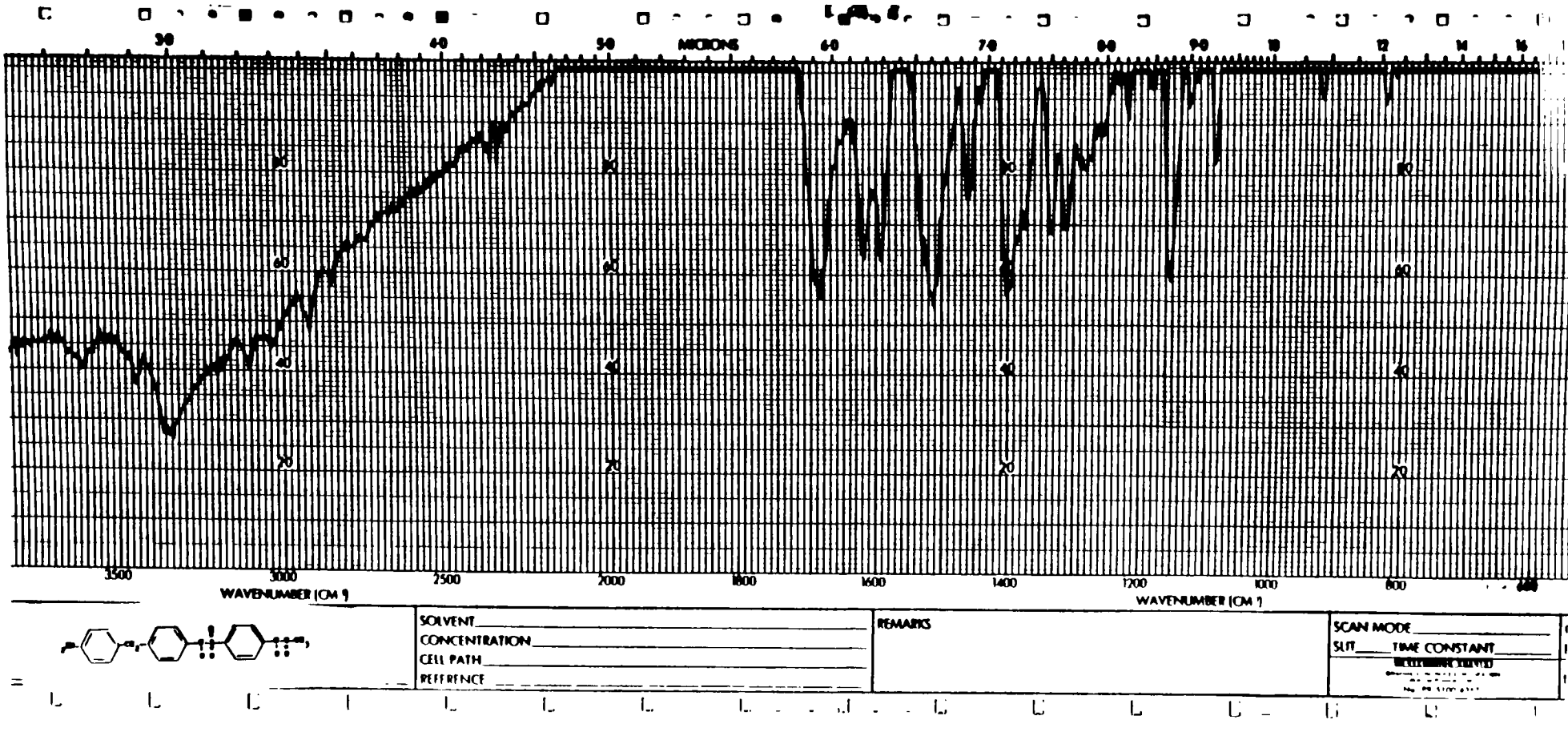


Figure 7: IR spectrum of monoacetanilide 17

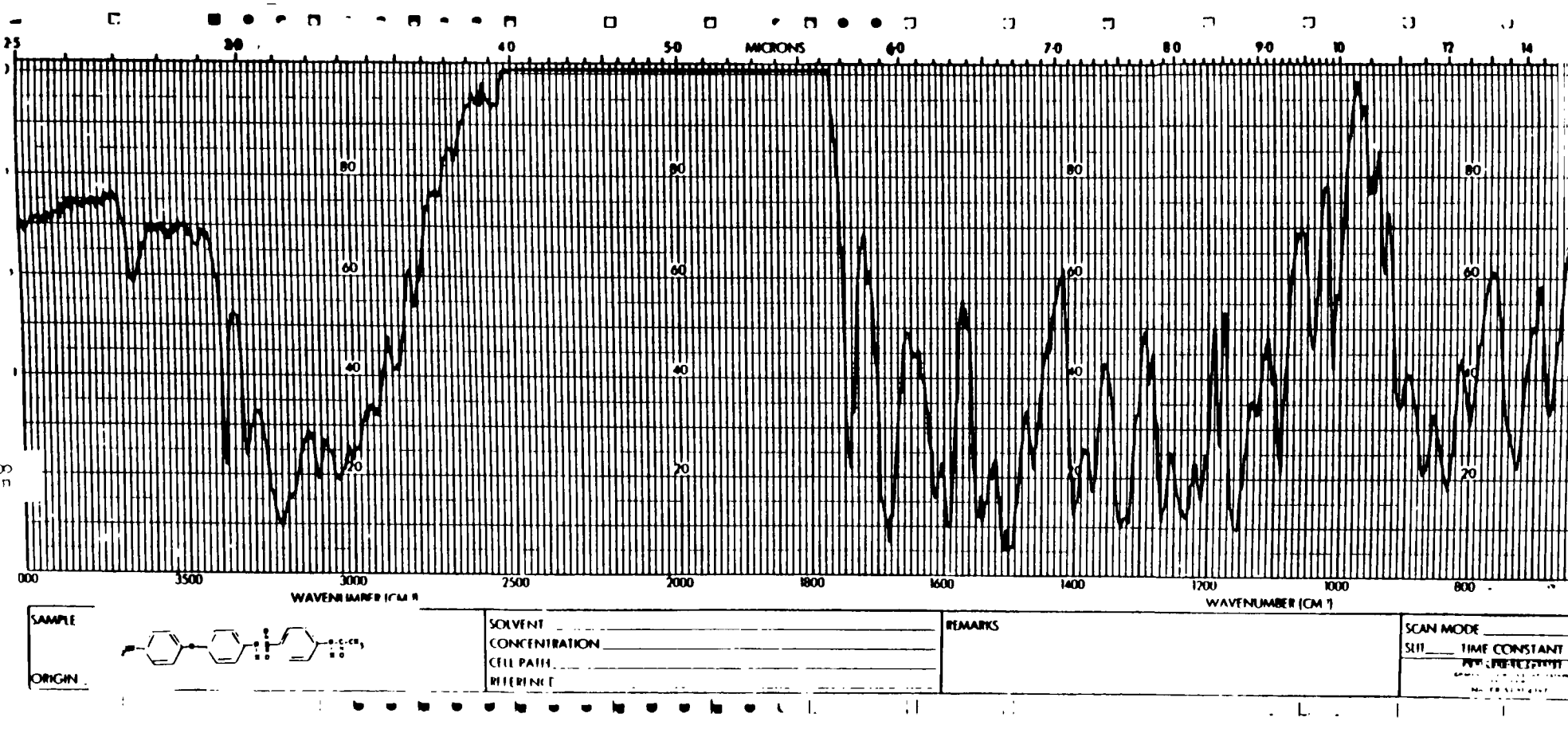


Figure 8: IR spectrum of monoacetanilide 18.

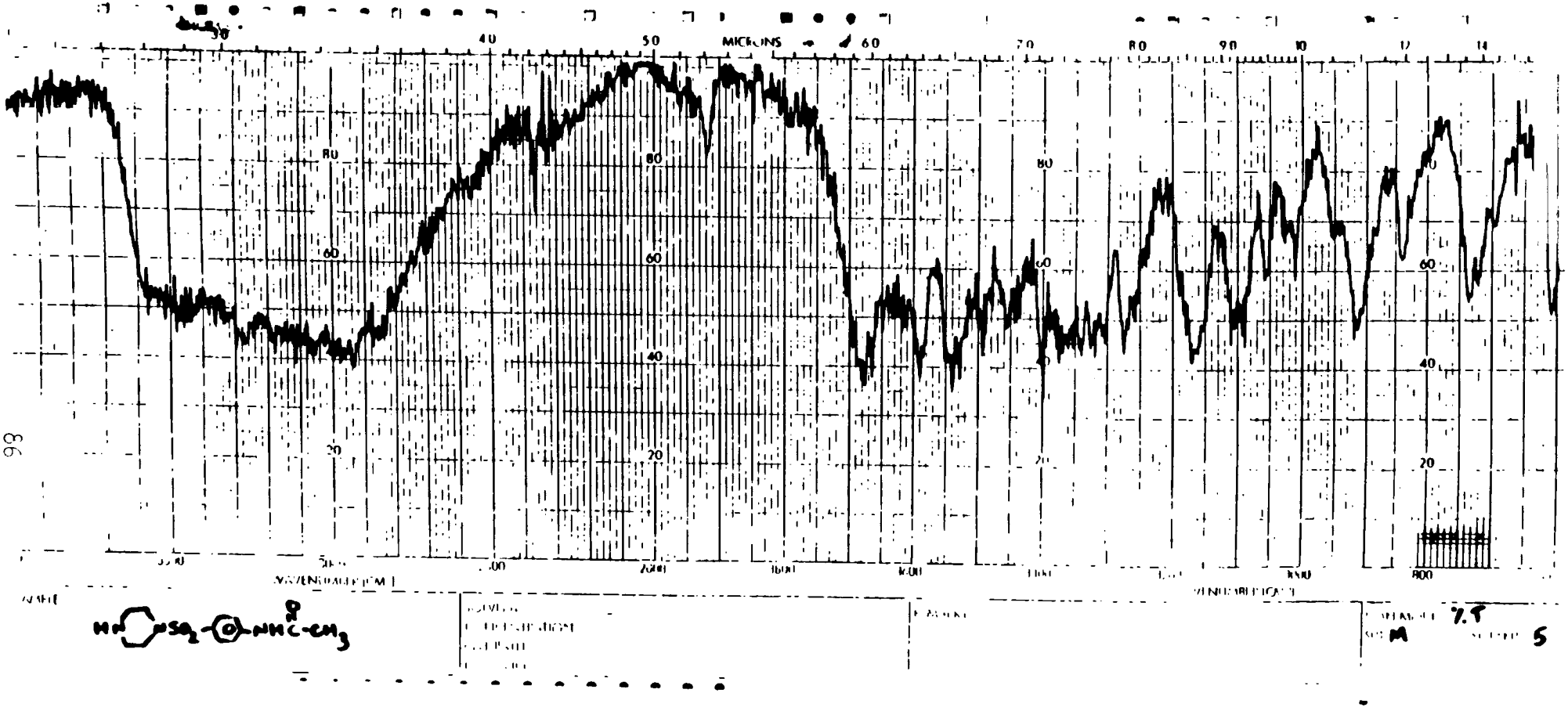


Figure 9: IR spectrum of monoacetanilide 19.

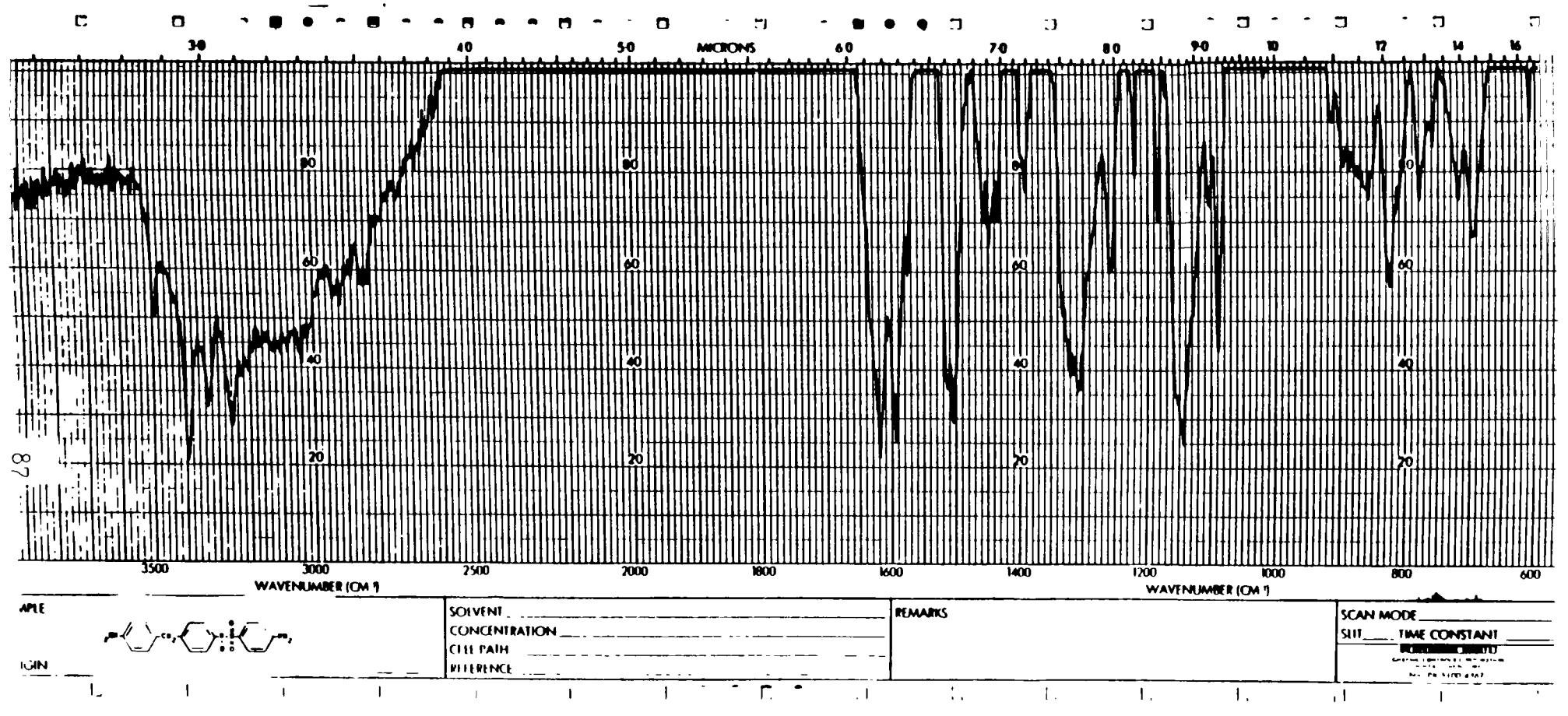


Figure 10: IR spectrum of diamine monomer 21.

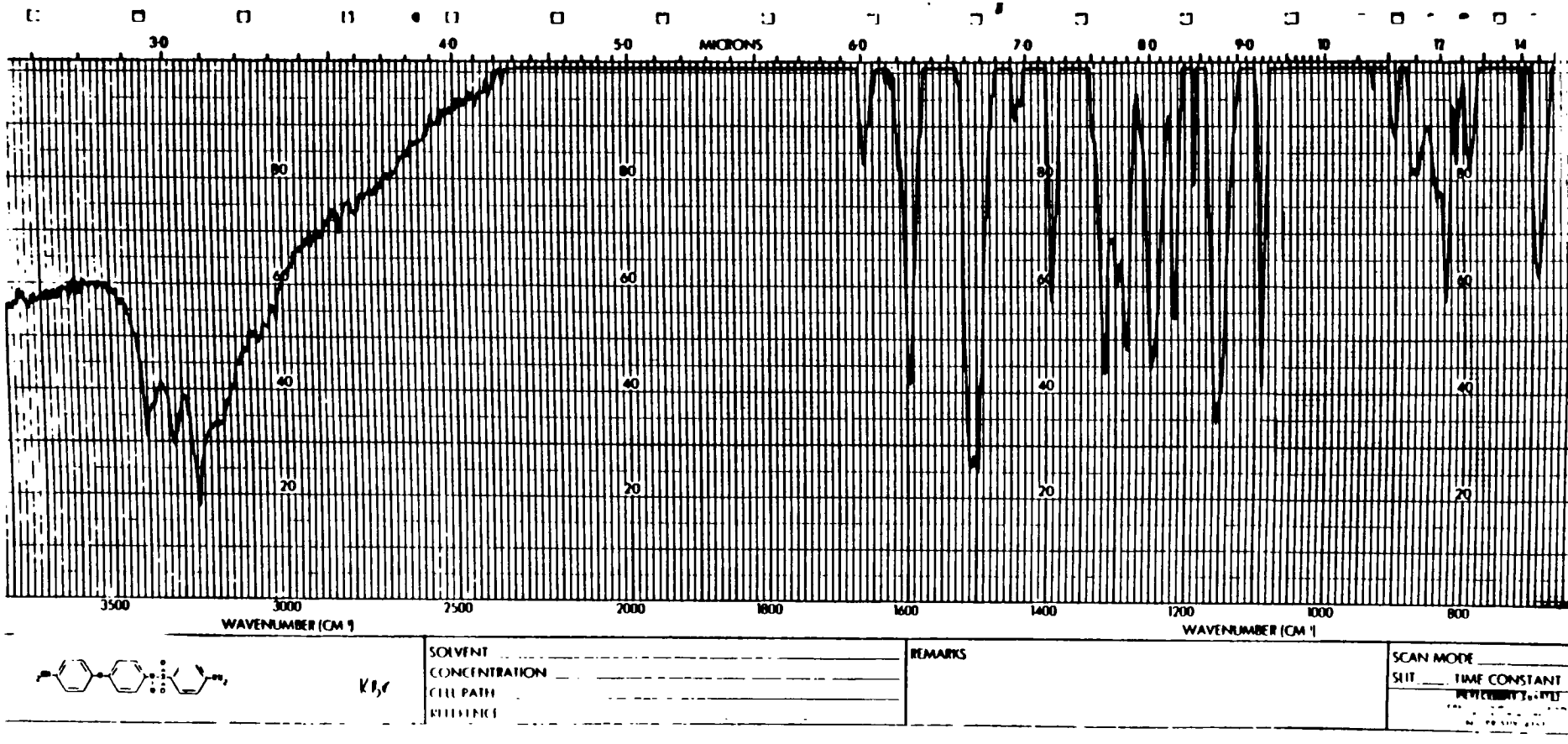


Figure 11: IR spectrum of diamine monomer 22.

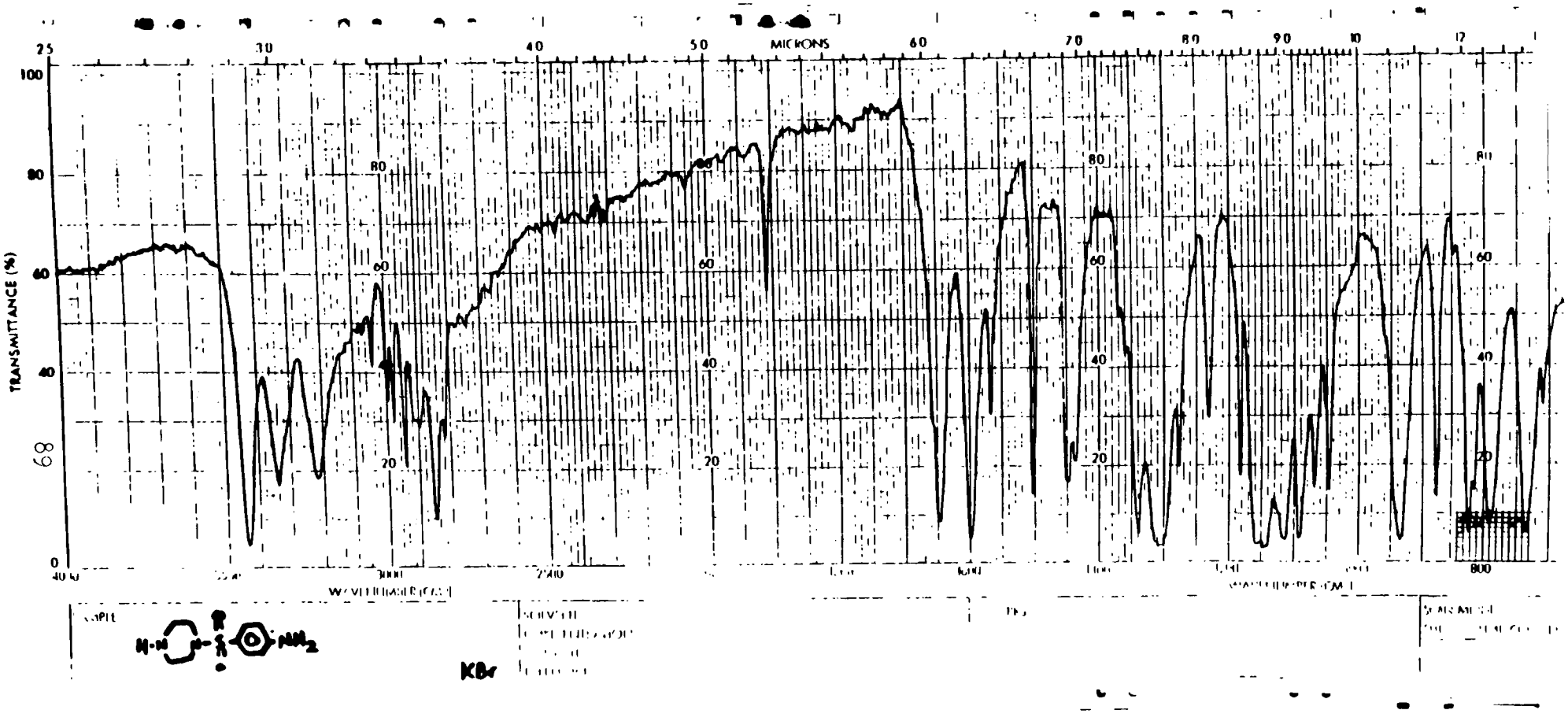


Figure 12: IR spectrum of diamine monomer 23.

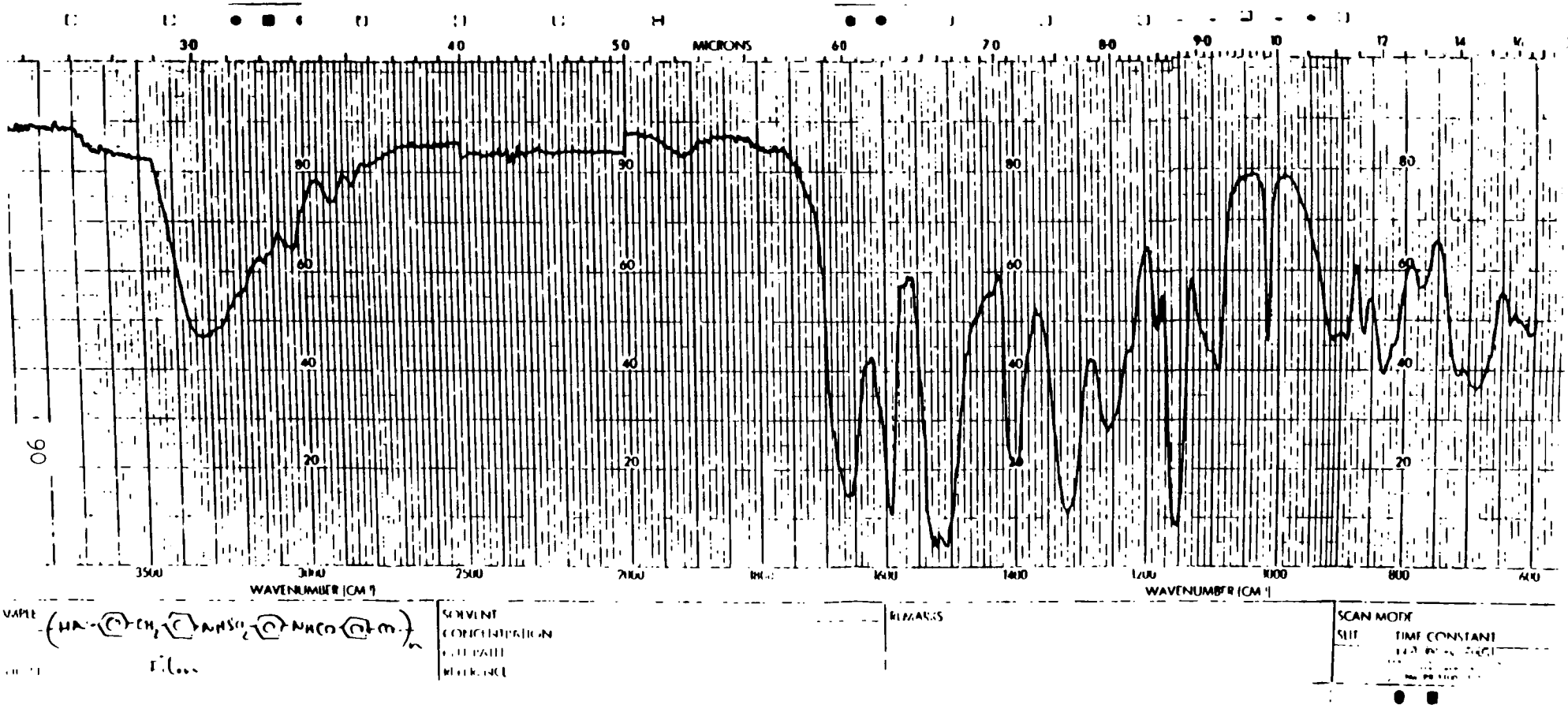


Figure 13: IR spectrum of poly(imino-1,4-phenylenesulfonyl-imino-1,4-phenylenemethylene-1,4-phenyleneimino-terephthaloyl) (MBST) 24.

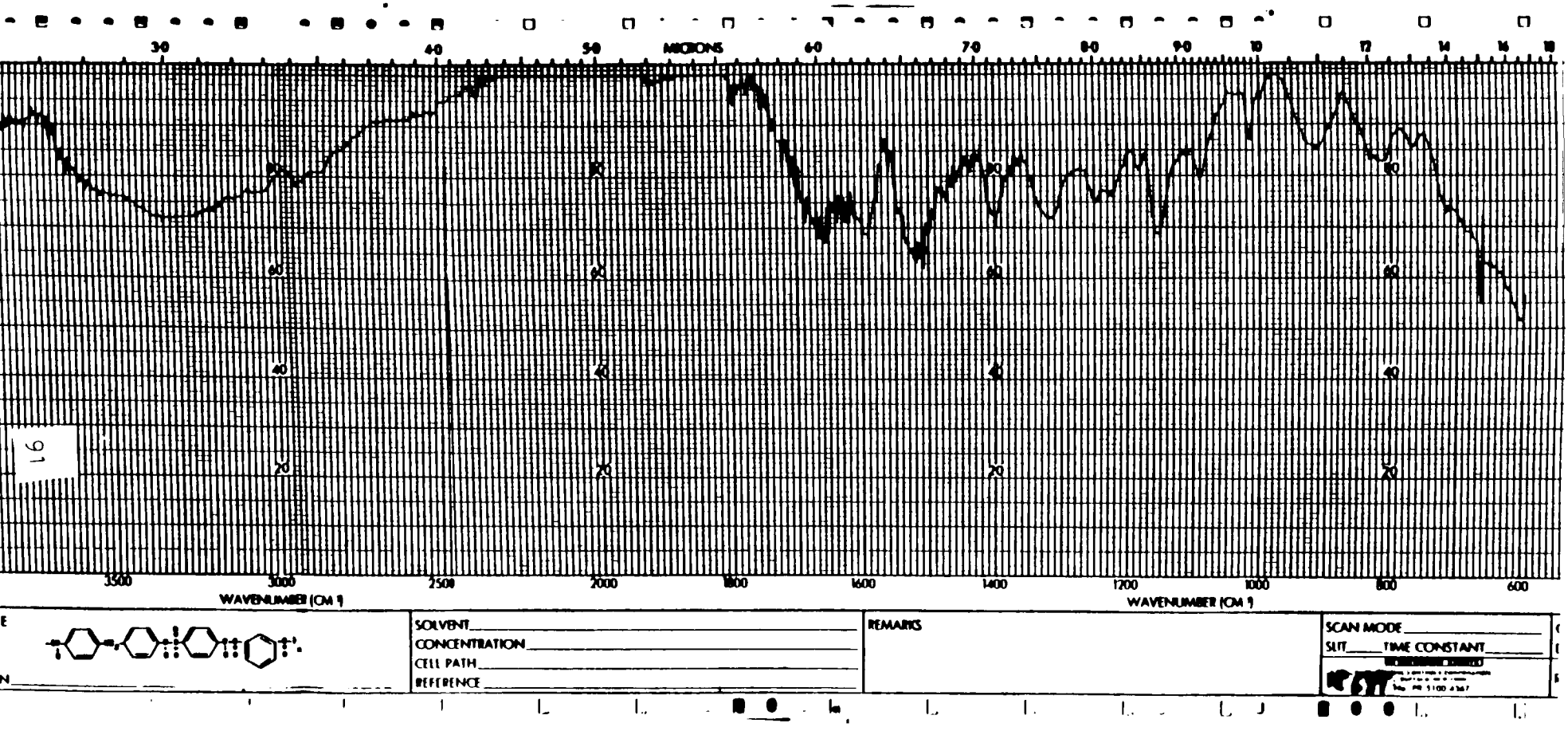


Figure 14: IR spectrum of poly(imino-1,4-phenylenesulfonyl-imino-1,4-phenylenemethylene-1,4-phenyleneimino-isophthaloyl) (MBSI) 25.

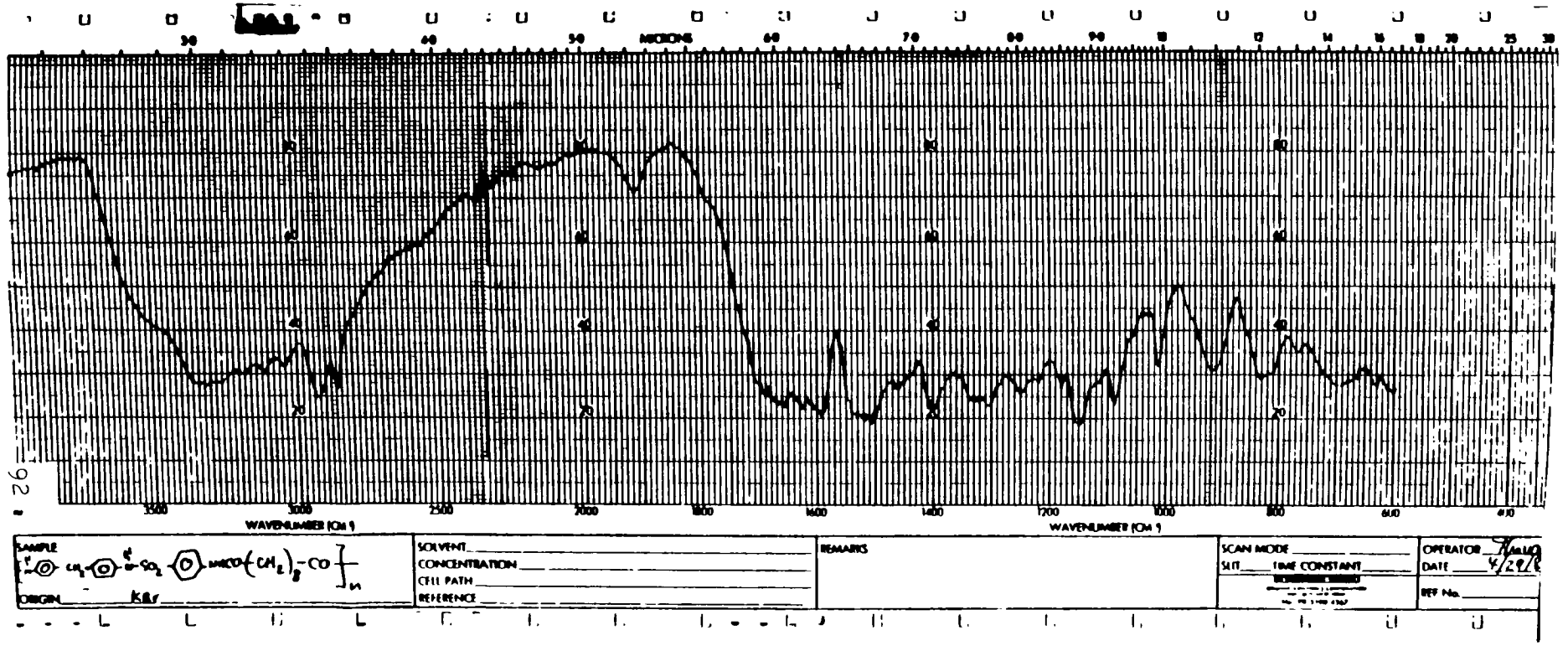


Figure 15: IR spectrum of poly(imino-1,4-phenylenesulfonylimino-1,4-phenylenemethylnene-1,4-phenyleneimino-sebacoyl) (MBSS) 26.

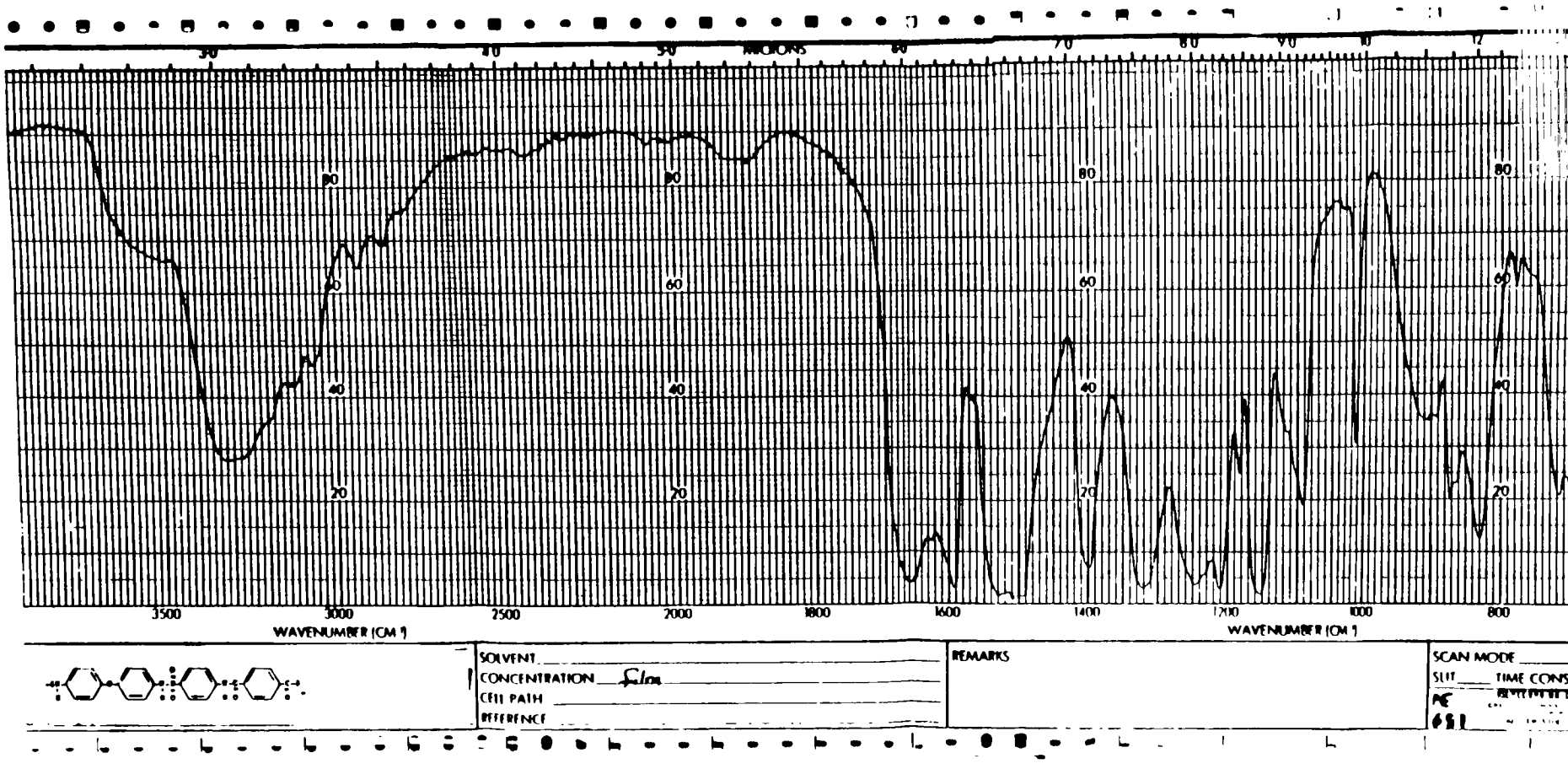


Figure 16: IR spectrum of poly(imino-1,4-phenylenesulfonylimino-1,4-phenylene-oxy-1,4-phenyleneiminoterephthaloyl) (OBST) 27.

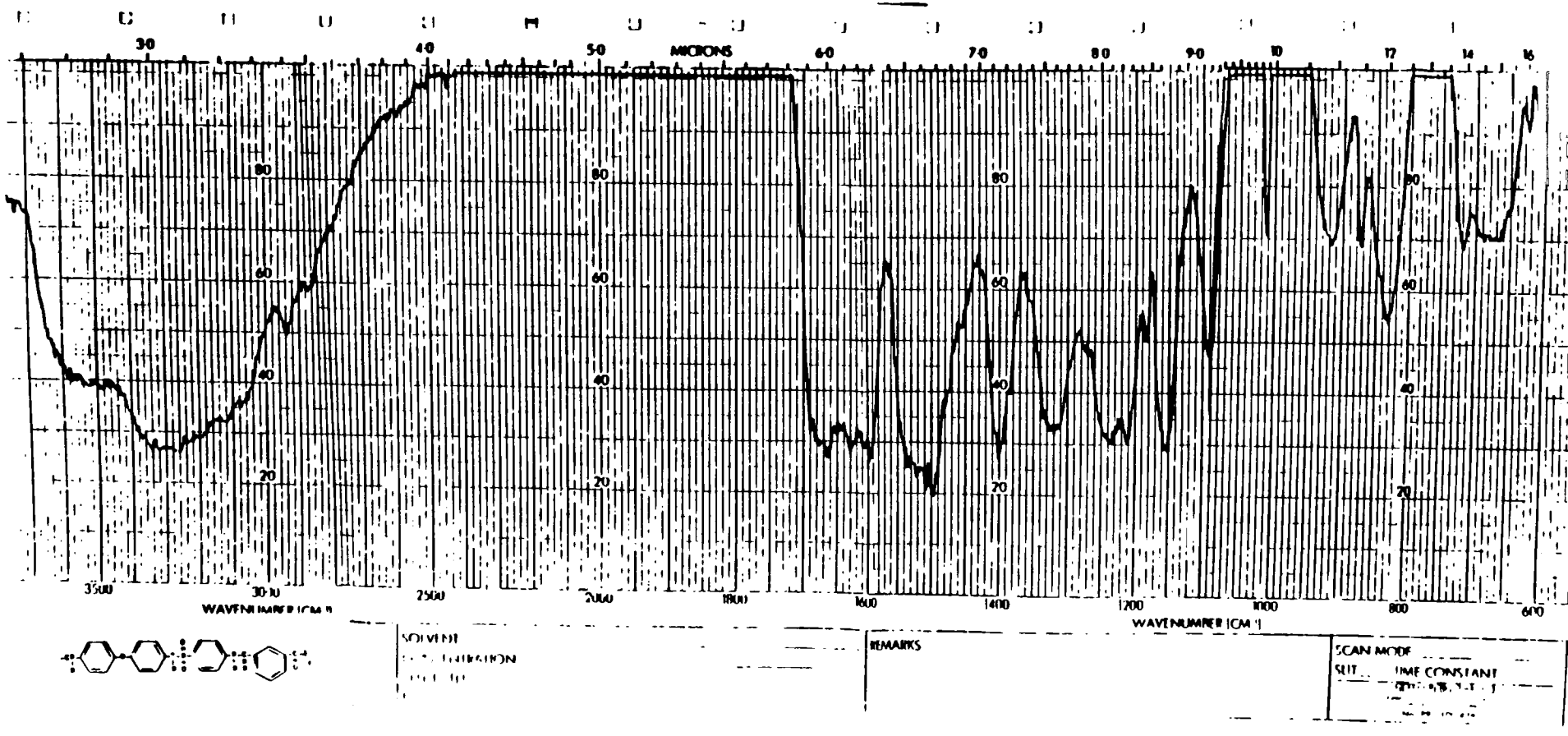


Figure 17: IR spectrum of poly(imino-1,4-phenylenesulfonylimino-1,4-phenylene-oxy-1,4-phenyleneiminoisophthaloyl) (OBSI) 28.

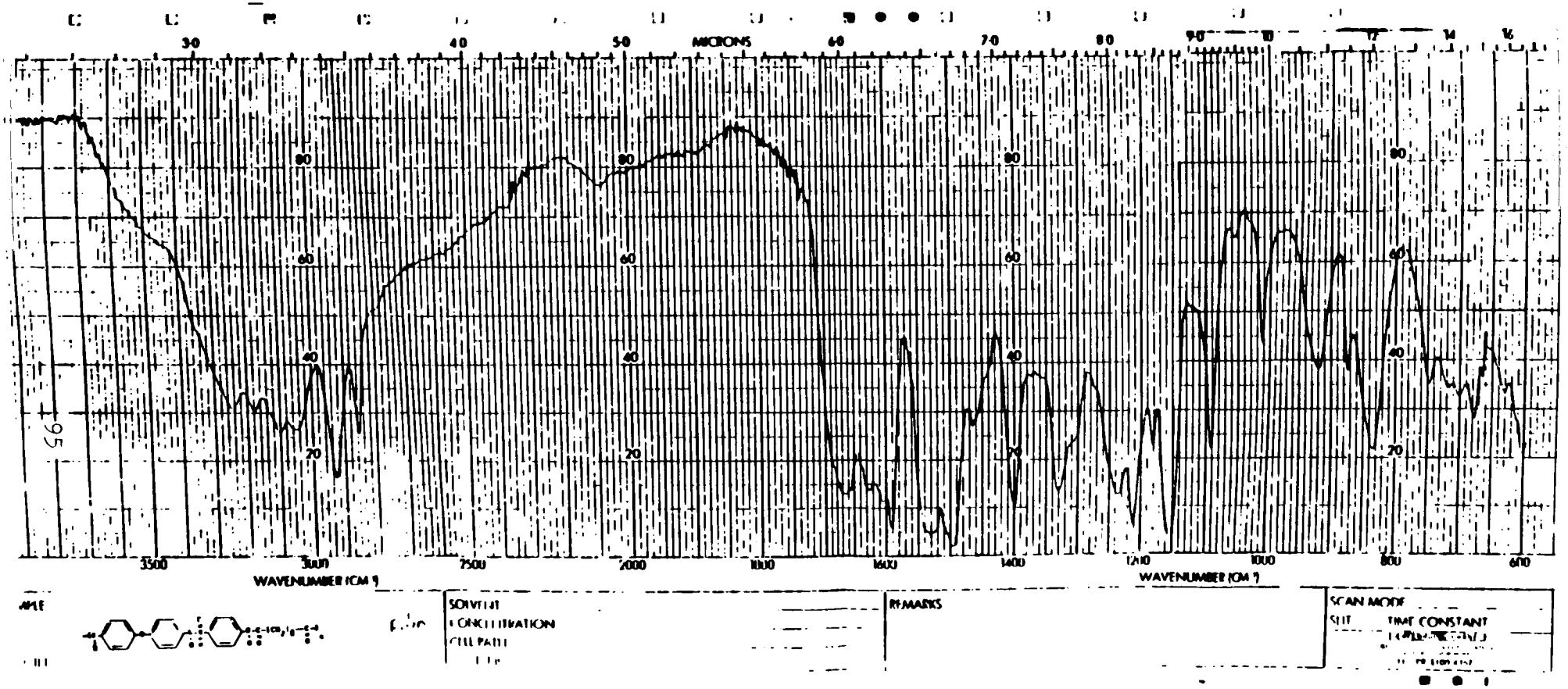


Figure 18: IR spectrum of poly(imino-1,4-phenylenesulfonylimino-1,4-phenylene-oxy-1,4-phenyleneiminosebacoyl) (OBSS) 29.

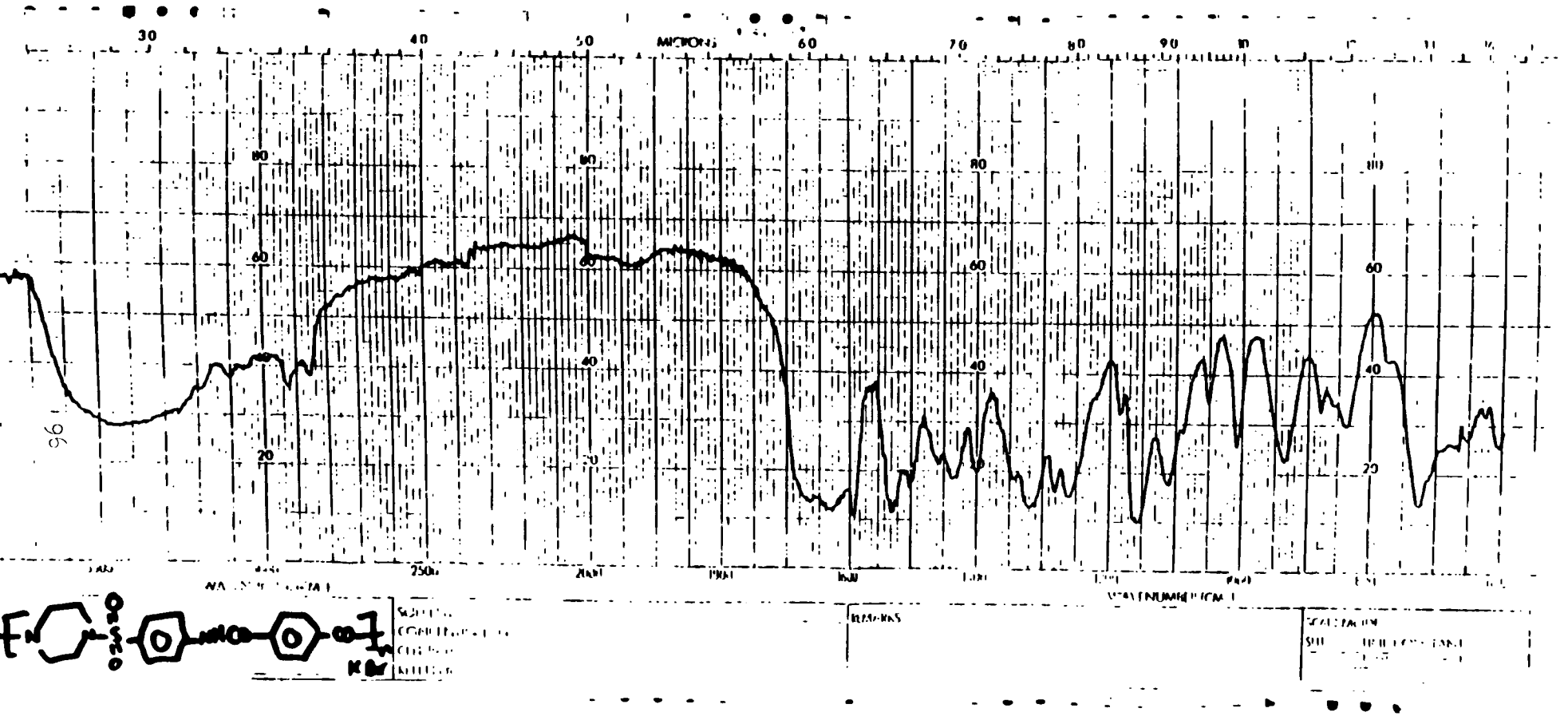


Figure 19: IR spectrum of poly(imino-1,4-phenylenesulfonyl-piperizinylene-terephthaloyl) (PBST) 30.

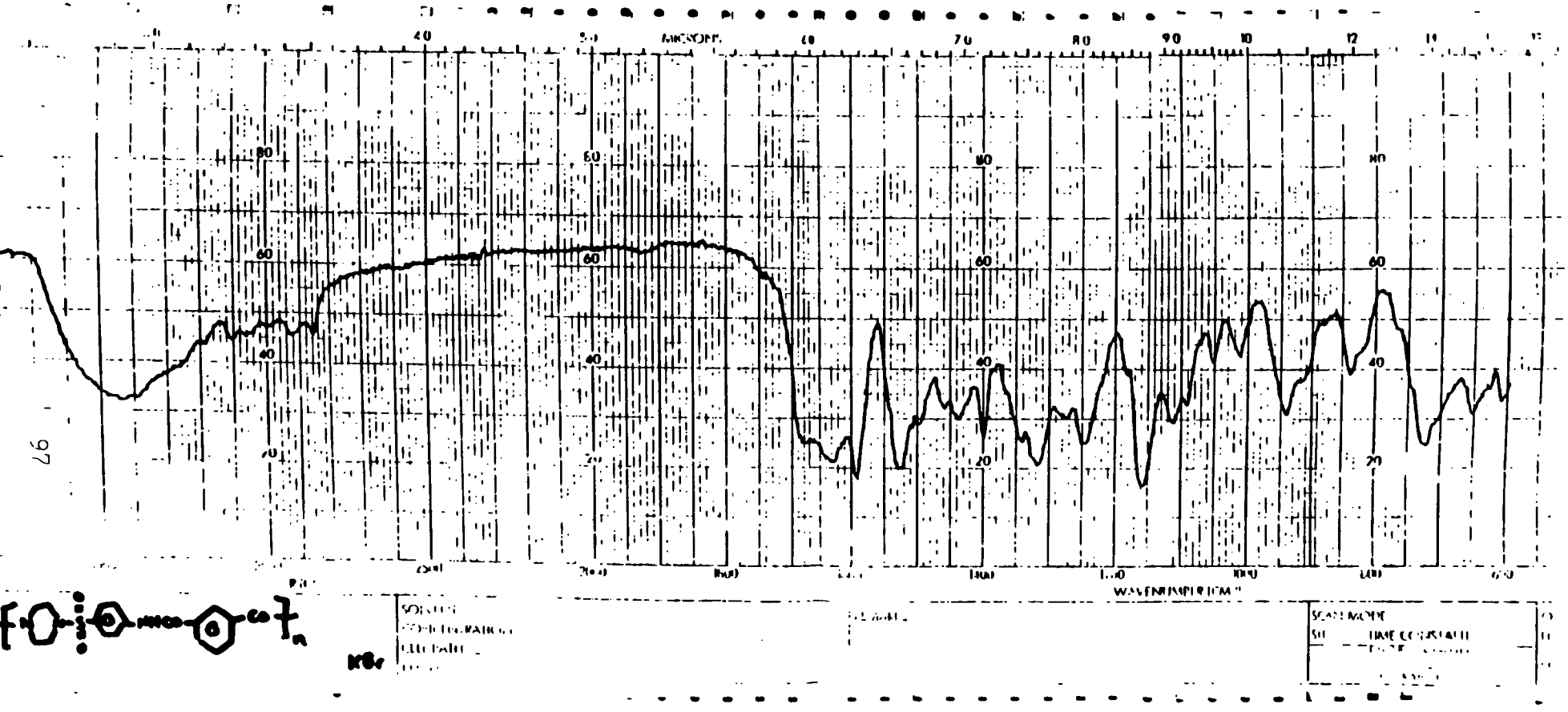


Figure 20: IR spectrum of poly(imino-1,4-phenylenesulfonyl-piperizinylene-isophthaloyl) (PBSI) 31.

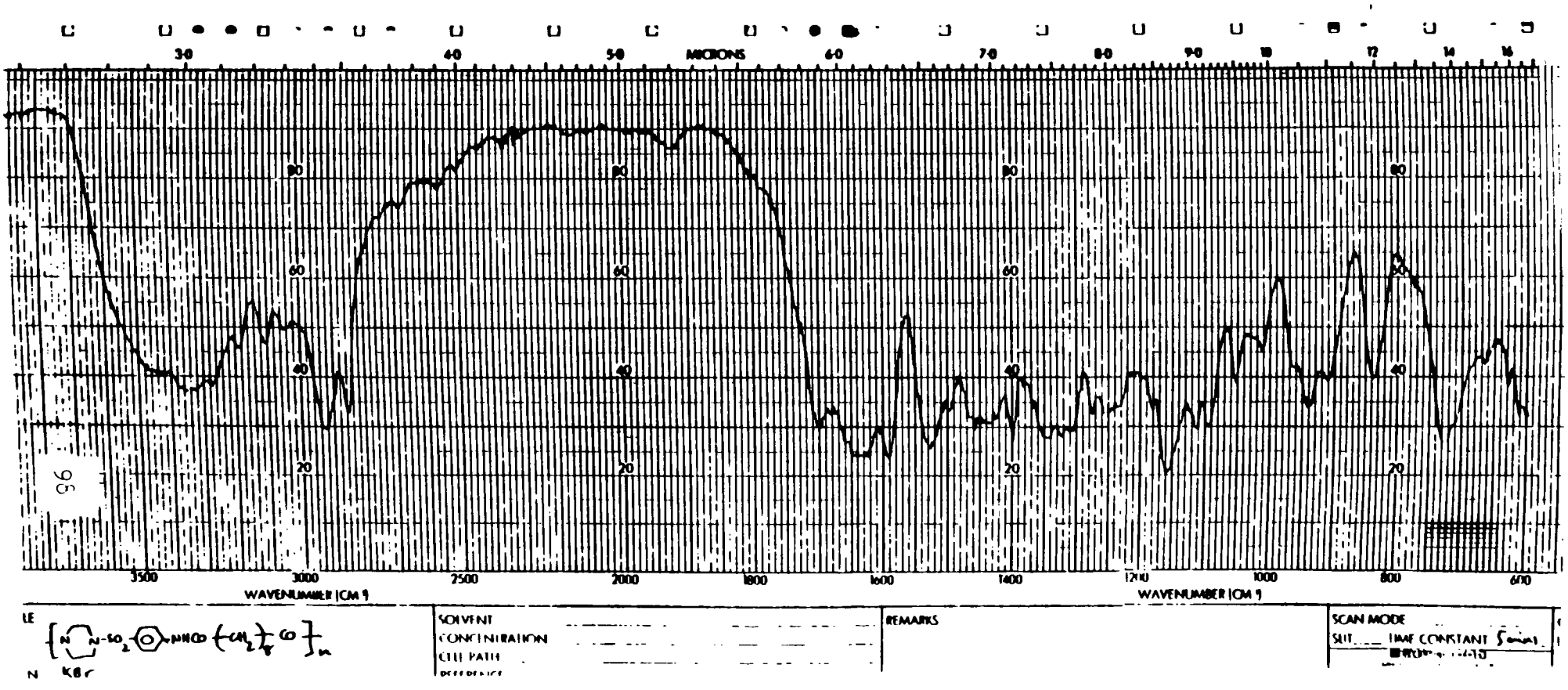


Figure 21: IR spectrum of poly(imino-1,4-phenylenesulfonyl-piperizinylne-sebacoyl) (PBSS) 32.

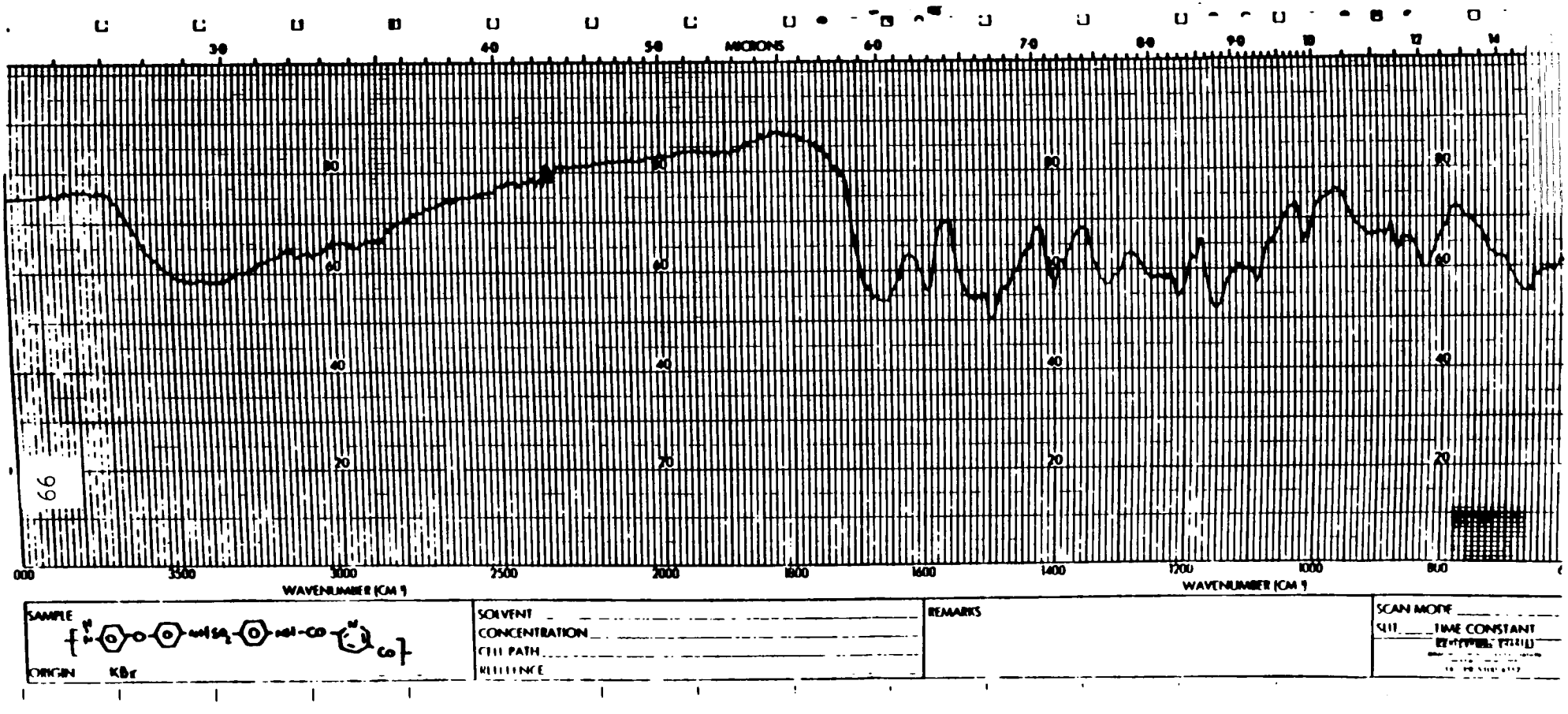


Figure 22: IR spectrum of poly(imino-1,4-phenylenesulfonylimino-1,4-phenyleneiminocarbonyl-2,5-pyridinediylcarbonyl) (OBSP) 33.

Figure 23: TGA curve of polymer 24.

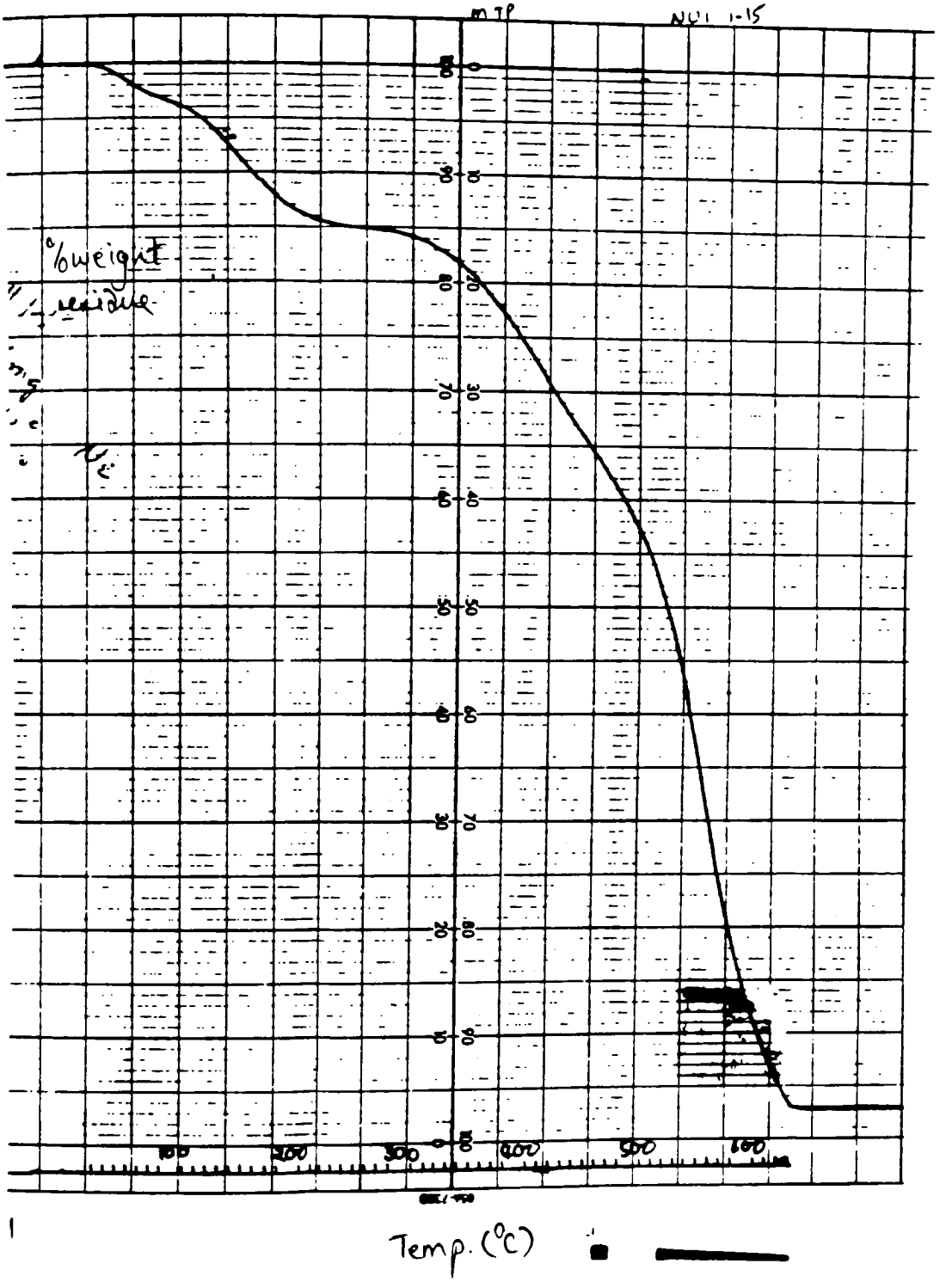


Figure 24: TGA curve of polymer 25.

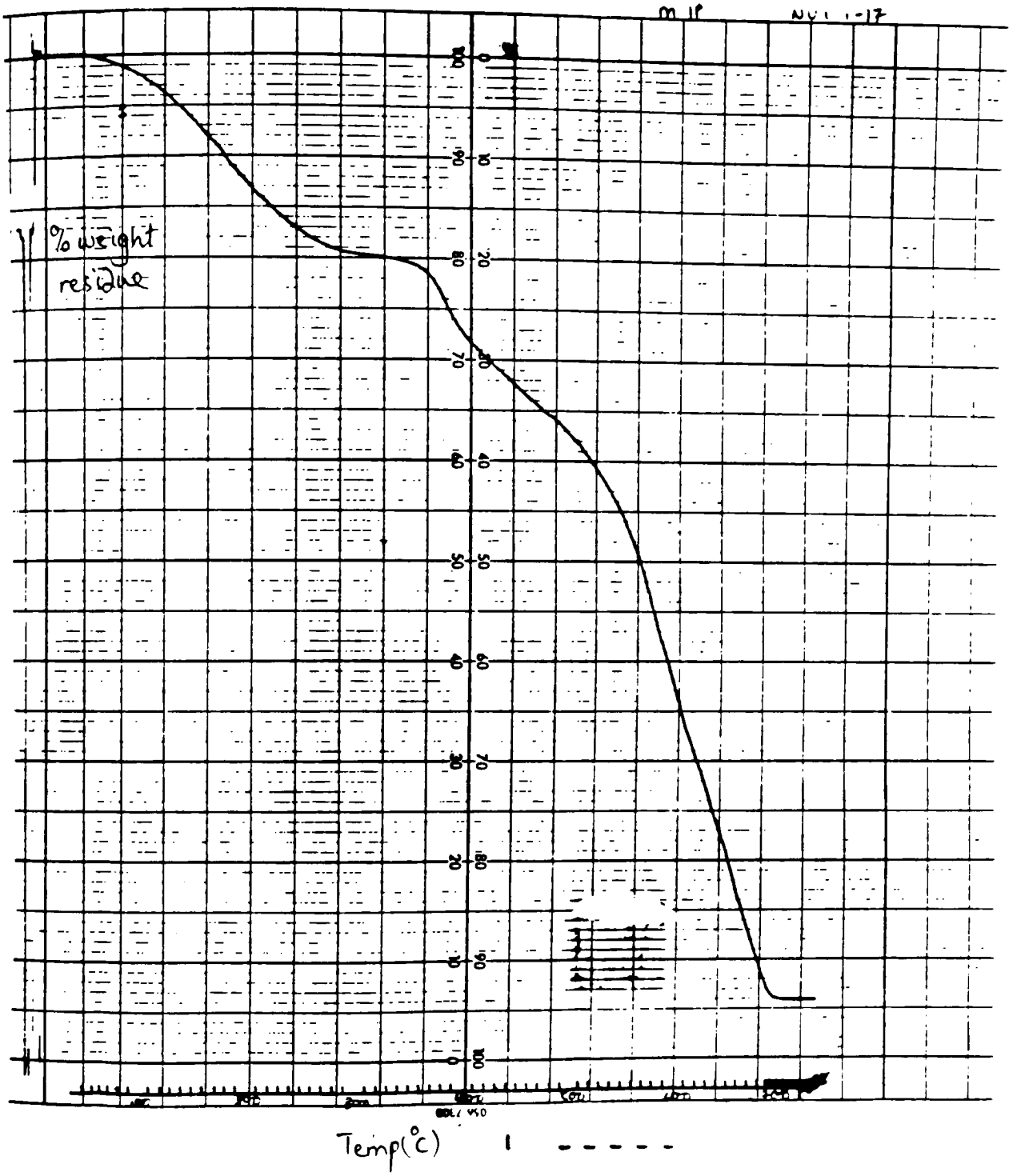


Figure 25: TGA curve of polymer 26.

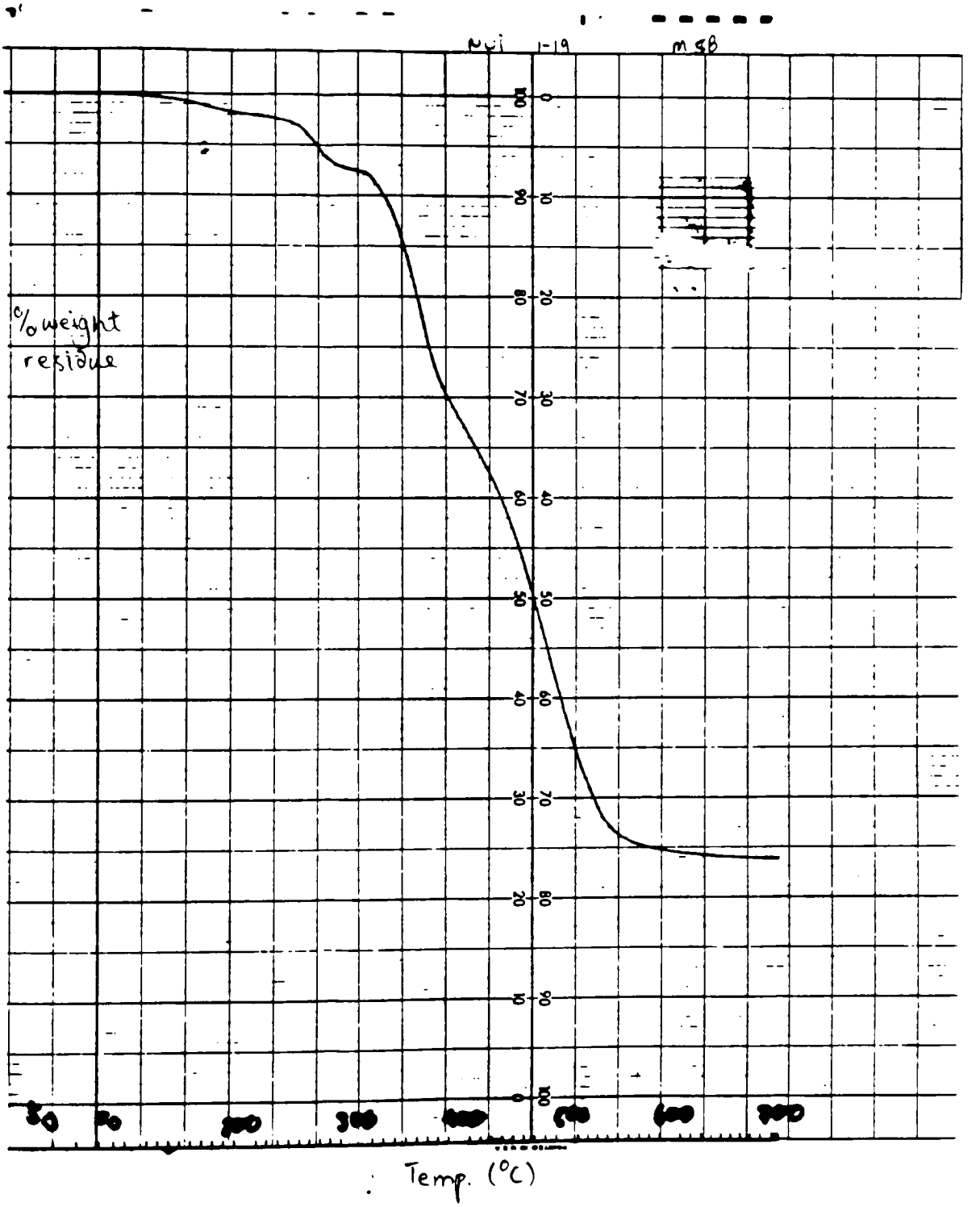


Figure 26: TGA curve of polymer 27.

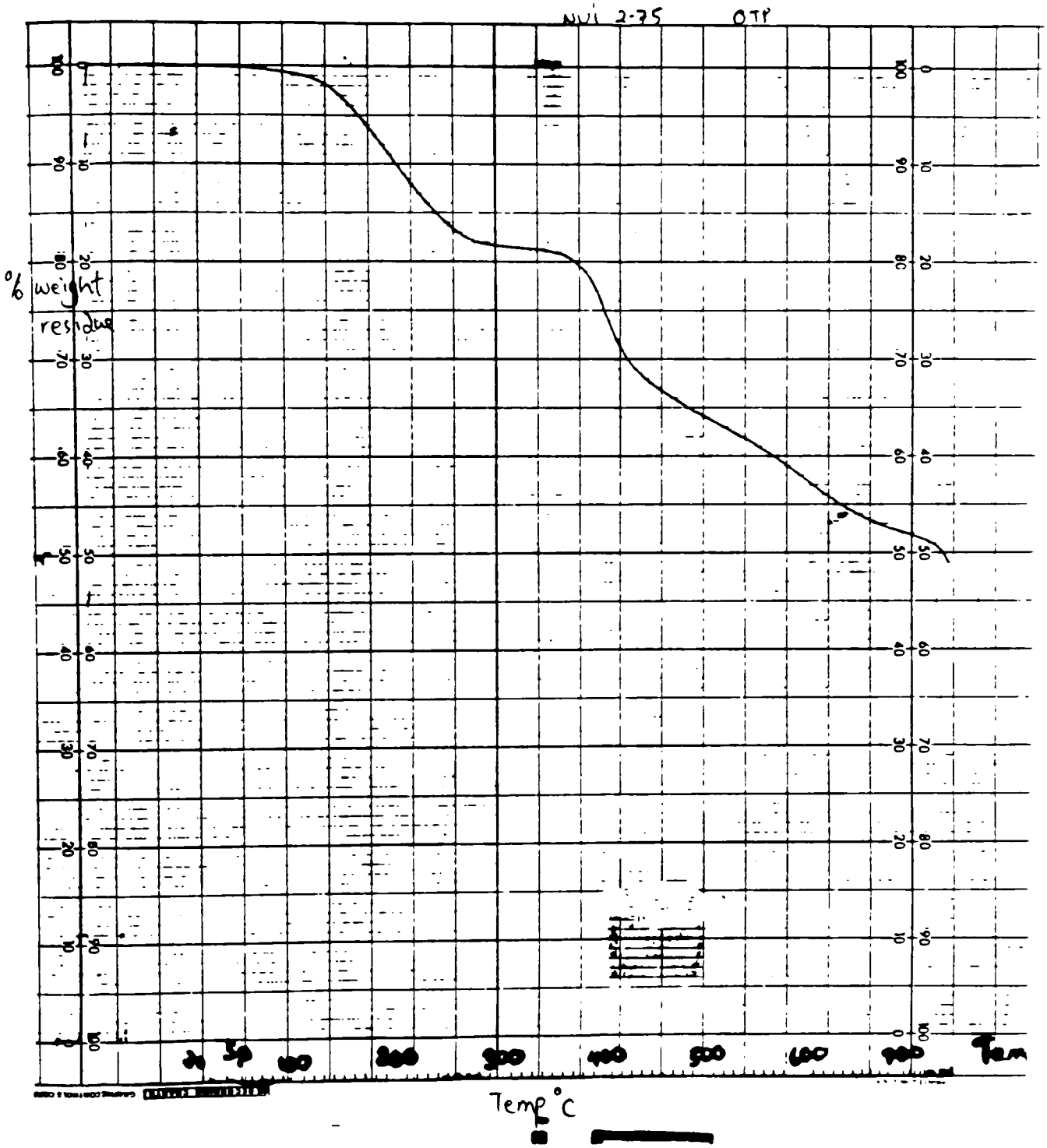


Figure 27: TGA curve of polymer 28.

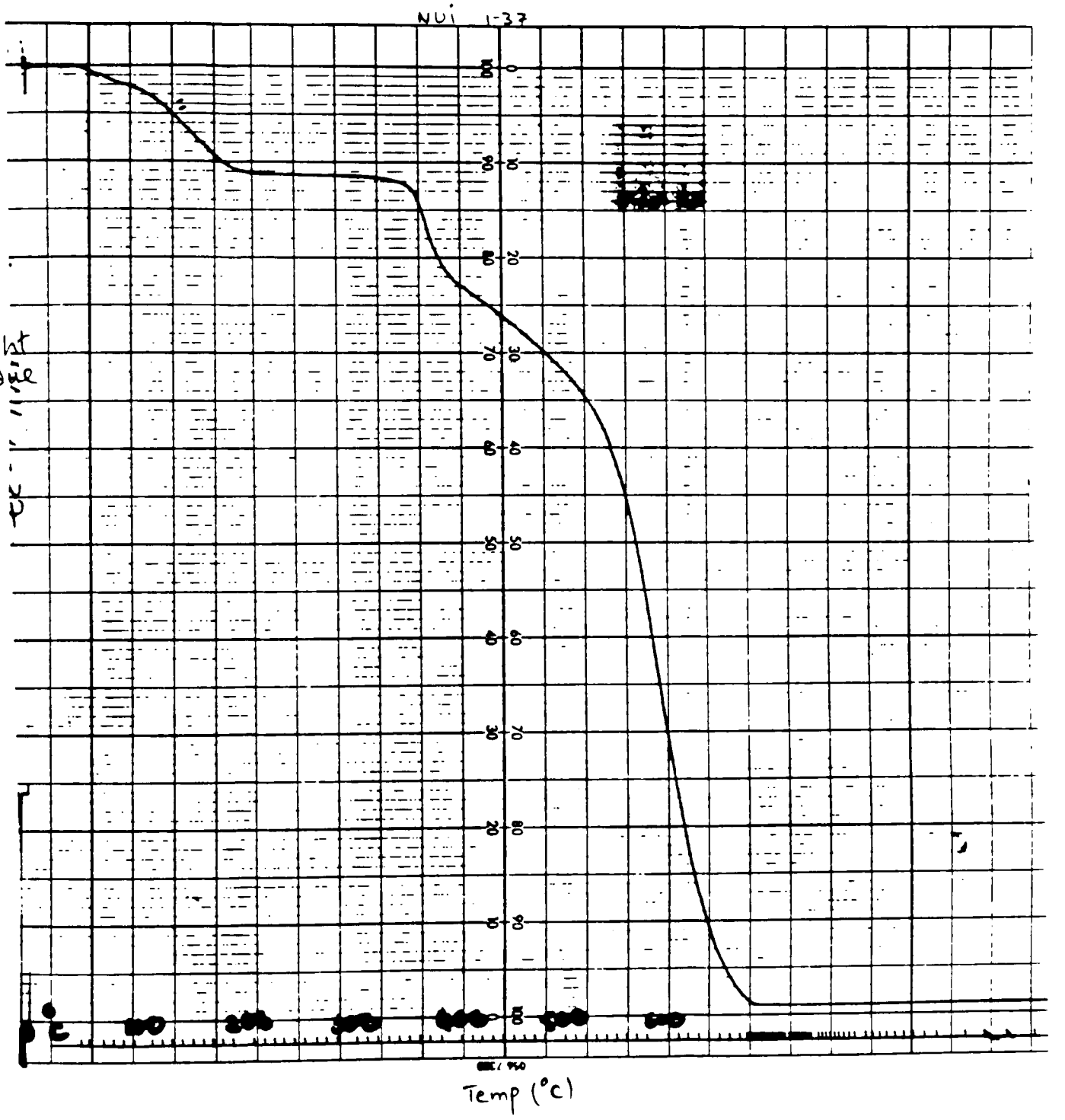


Figure 28: TGA curve of polymer 29.

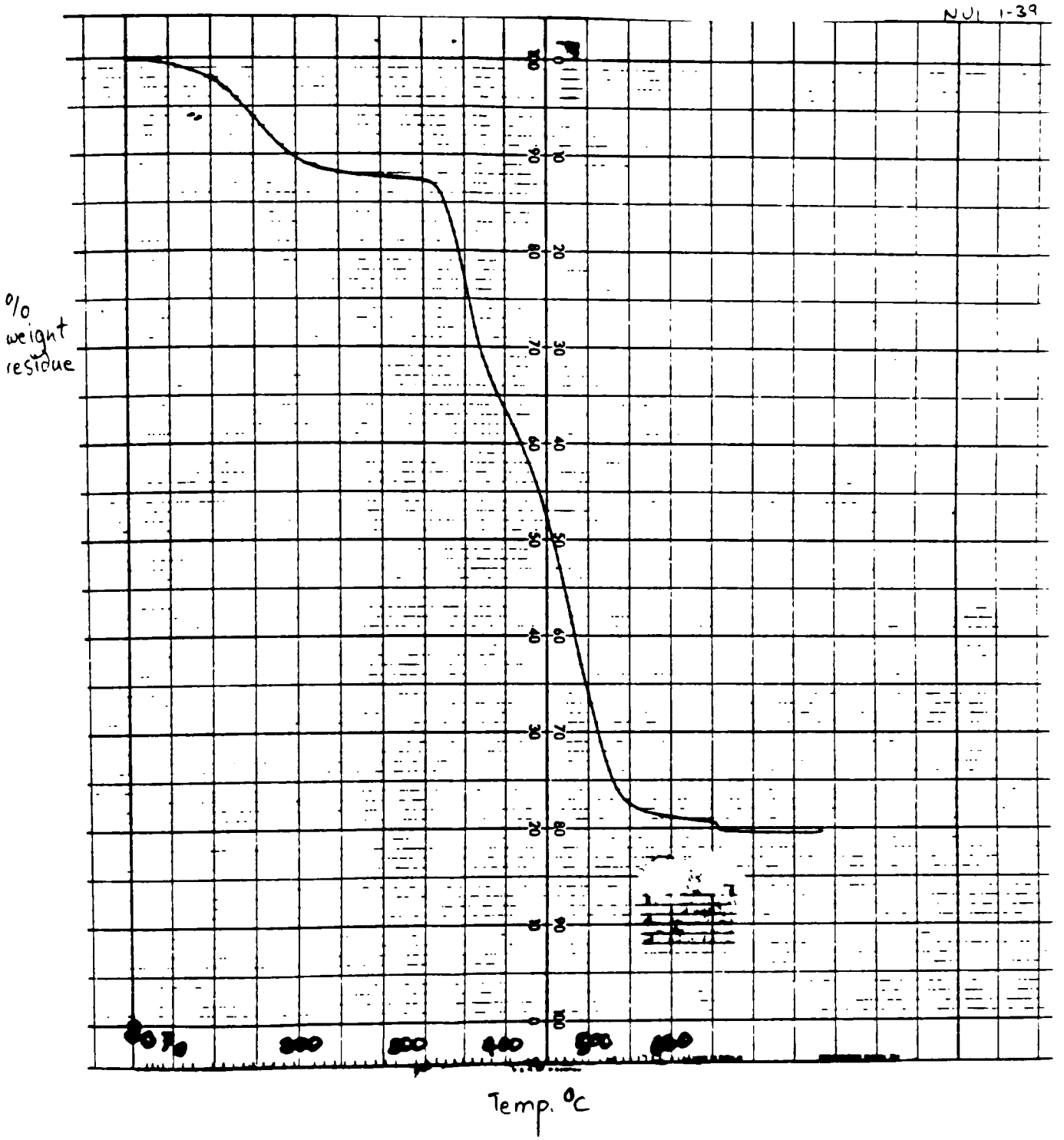


Figure 29: TGA curve of polymer 30.

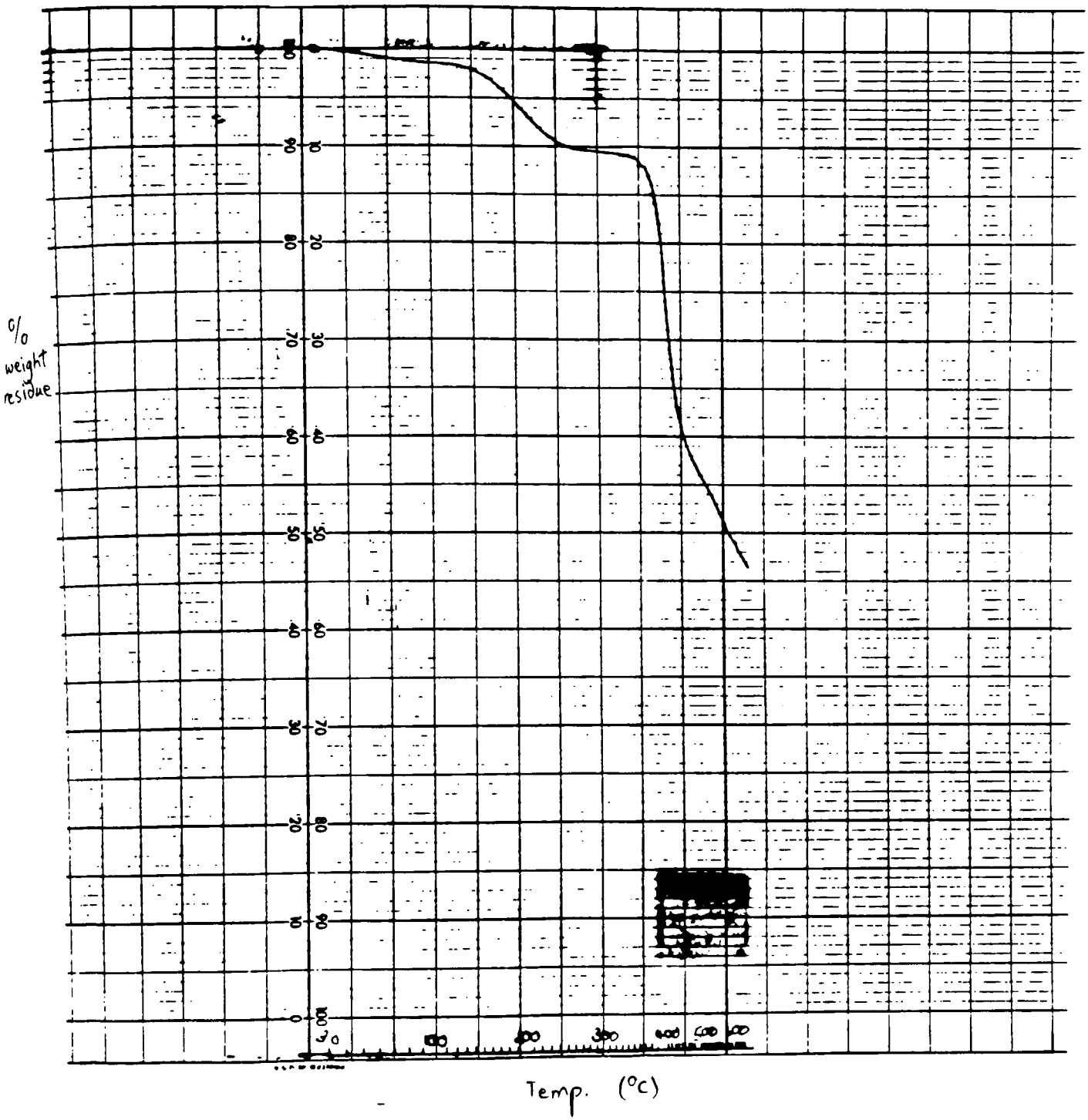
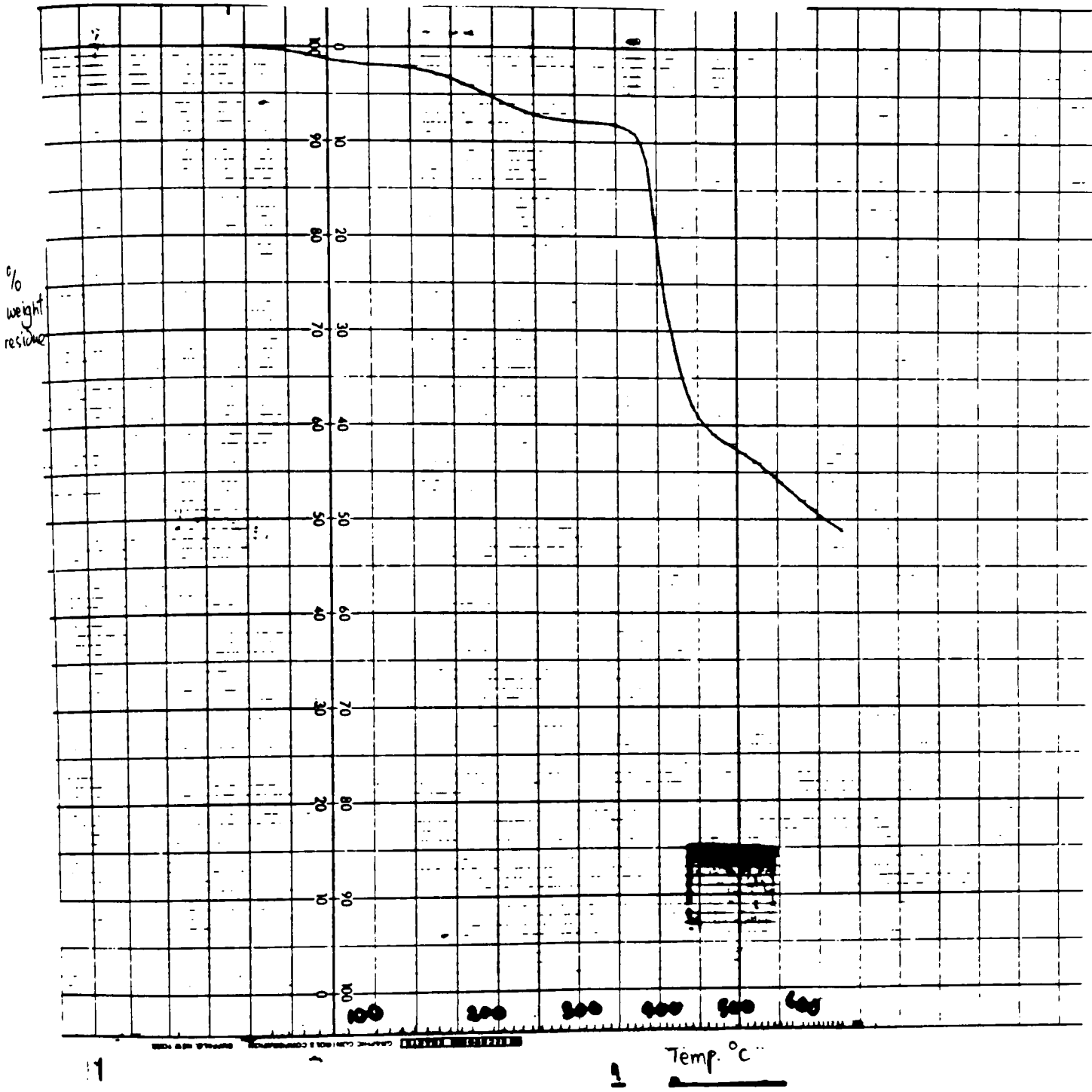


Figure 30: TGA curve of polymer 31



e 31: TGA curve of polymer 32.

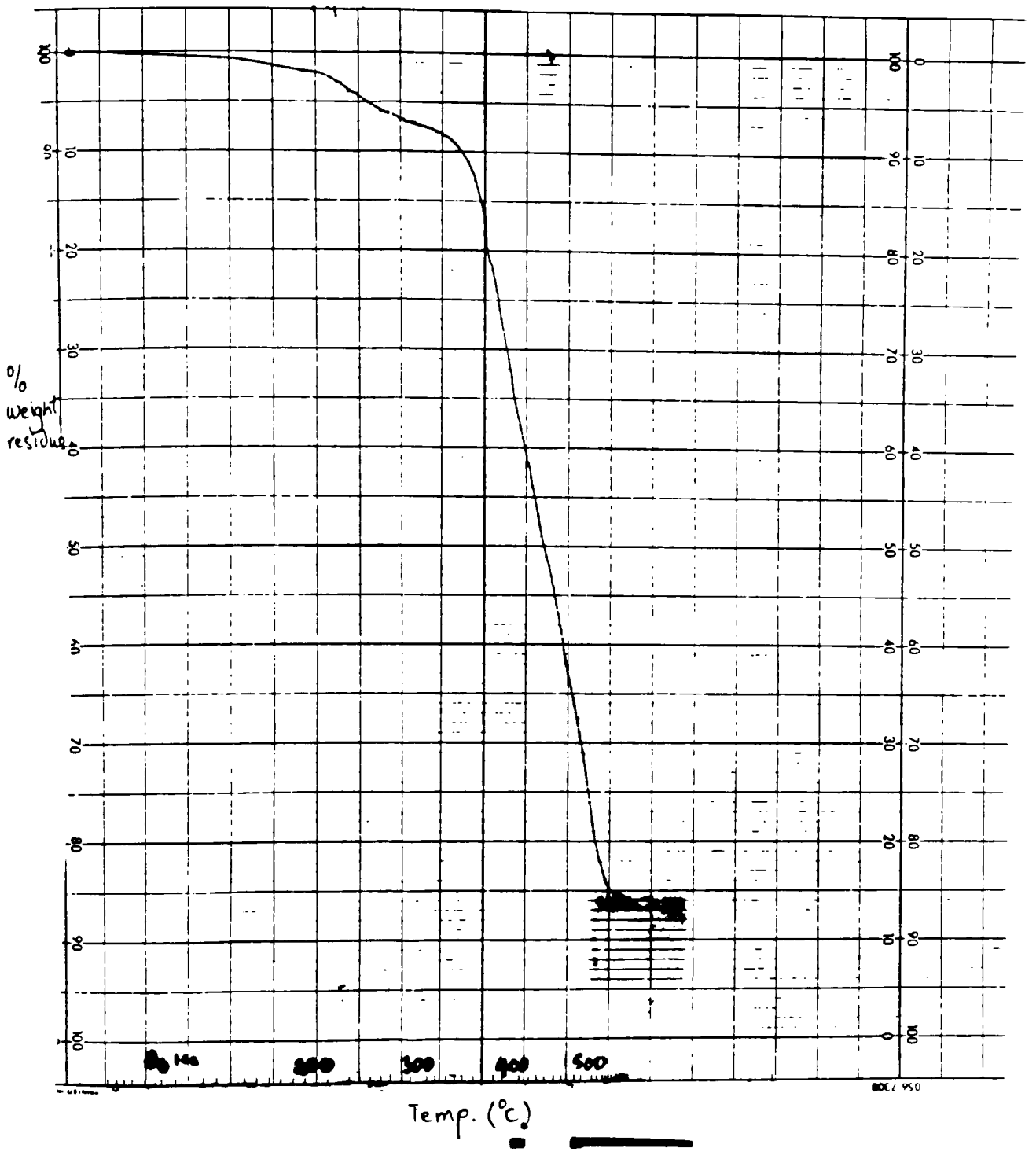


Figure 32: TGA curve of polymer 33.